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(54) **Chemically amplified positive resist composition and patterning method**

(57) A chemically amplified positive resist composition comprising a base resin and a compound containing two to six functional groups, specifically alkenyloxy,

acetal and ortho-ester groups in the molecule is suitable for forming a contact hole pattern by the thermal flow process.

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Description**TECHNICAL FIELD**

- 5 **[0001]** This invention relates to a chemically amplified positive resist composition for forming a contact hole pattern by the thermal flow process. While a method for forming a contact hole pattern using a chemically amplified positive resist composition comprising a polymer as the base resin involves the thermal flow step of heat treating the contact hole pattern for further reducing the size of contact holes, the invention relates to the resist composition to which a compound having functional groups capable of crosslinking with the polymer is added so that the size reduction by thermal flow becomes easy to control. The invention also relates to a method for forming a microsize contact hole pattern in the manufacture of VLSIs.

BACKGROUND ART

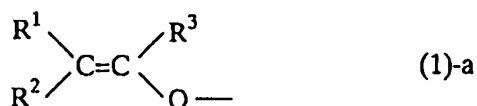
- 15 **[0002]** While a number of recent efforts are being made to achieve a finer pattern rule in the drive for higher integration and operating speeds in LSI devices, deep-ultraviolet lithography is thought to hold particular promise as the next generation in microfabrication technology. Deep-UV lithography is capable of achieving a minimum feature size of 0.3 μm or less and, when a resist having low light absorption is used, can form patterns with sidewalls that are nearly perpendicular to the substrate.
- 20 **[0003]** Recently developed acid-catalyzed chemically amplified positive resists, such as those described in JP-B 2-27660, JP-A 63-27829, USP 4,491,628 and USP 5,310,619, utilize a high-intensity KrF or ArF excimer laser as the deep-UV light source. These resists, with their excellent properties such as high sensitivity, high resolution, and good dry etching resistance, are especially promising for deep-UV lithography.
- 25 **[0004]** Such chemically amplified positive resist compositions include two-component systems comprising a base resin and a photoacid generator, and three-component systems comprising a base resin, a photoacid generator, and a dissolution regulator having acid labile groups.
- 30 **[0005]** For example, JP-A 62-115440 describes a resist composition comprising poly-4-tert-butoxystyrene and a photoacid generator, and JP-A 3-223858 describes a similar two-component resist composition comprising a resin bearing tert-butoxy groups within the molecule, in combination with a photoacid generator. JP-A 4-211258 describes a two-component resist composition which is comprised of polyhydroxystyrene bearing methyl, isopropyl, tert-butyl, tetrahydropyranyl, and trimethylsilyl groups, together with a photoacid generator.
- 35 **[0006]** JP-A 6- 100488 discloses a resist composition comprising a polydihydroxystyrene derivative, such as poly[3,4-bis(2-tetrahydropyranyloxy)styrene], poly[3,4-bis(tert-butoxycarbonyloxy)styrene] or poly[3,5-bis(2-tetrahydropyranyloxy)styrene], and a photoacid generator.
- 40 **[0007]** Improvement and development efforts have been continuously made on the base resin in resist compositions of this type. JP-A 10-207066 discloses a resist composition comprising a base resin which is crosslinked with crosslinking groups having C-O-C linkages and a photoacid generator wherein the crosslinking groups are eliminated under the action of acid generated from the photoacid generator upon exposure, achieving a high contrast and high resolution.
- 45 **[0008]** Even when any base resin designed to enhance the resolving power is used in such chemically amplified positive resist compositions, it is yet difficult to reach a contact hole size of 0.20 μm or less. There are available no resist compositions for forming a contact hole pattern satisfying the requirement of LSI devices of the next generation.
- 50 **[0009]** On the other hand, the known technology of forming a contact hole size of 0.20 μm or less is to heat treat a contact hole pattern for causing the resist film to flow and reducing the contact hole size. This technology is known as thermal flow process. The use of the thermal flow process enables formation of a miniature contact hole size as fine as 0.10 μm or 0.15 μm .
- 55 **[0010]** In forming microsize contact holes by the thermal flow process, however, it is very difficult to control the heat treating temperature so as to provide a shrinkage matching with the desired contact hole size. That is, the thermal flow process has the drawback that even a slight variation of heating temperature brings about a substantial variation of contact hole size.
- 60 **[0011]** Referring to FIG. 1, there is illustrated in cross section a resist film 2 on a substrate 1, a contact hole 3 being formed through the resist film 2. The contact hole having undergone the thermal flow process has a profile as shown in FIG. 1, that is, a cross-sectional profile bowed at corners. The thermal flow process also has the problem that the profile of a contact hole is deteriorated.

SUMMARY OF THE INVENTION

- [0012]** An object of the invention is to provide a novel and improved chemical amplification type, positive working resist composition which has controllable process adaptability relative to the heat treating temperature when a microsize

contact hole pattern is conventionally formed by the thermal flow process, and thus has satisfactory practical utility. Another object is to provide a novel and improved method for forming a contact hole pattern.

[0013] It has been found that when a contact hole pattern is formed by the thermal flow process using a chemically amplified positive resist composition comprising a compound containing at least two functional groups of the general formulas (1)-a to (1)-c in a molecule, the overall method is improved in process control and thus practically acceptable.



Herein R¹ to R⁴ are hydrogen or straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, R⁵ to R⁹ are independently straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, and a pair of R¹ and R³, a pair of R⁴ and R⁵, a pair of R⁵ and R⁶, a pair of R⁷ and R⁸, a pair of R⁷ and R⁹ or a pair of R⁸ and R⁹, taken together, may form a ring. For brevity sake, formulas (1)-a to (1)-c are sometimes referred to as formula (1), hereinafter.

[0014] Specifically, making the investigations to be described below, the inventor has established the method of controlling the thermal flow process.

[0015] In the inventor's experiment, a variety of base resins commonly used in conventional chemically amplified positive resist compositions were used to form resist films, which were provided with contact holes and subjected to the thermal flow process. The contact hole size was plotted relative to the heating temperature in a graph. It was found that the slope representing a change of contact hole size (to be referred to as a flow rate, hereinafter) was not so different among different base resins. Namely, changing the base resin skeleton gives no substantial difference in the flow rate. The flow rate remains substantially unchanged whether the base resin is a homopolymer or a copolymer and when the molecular weight or dispersity of the base resin is changed. This is also true when the acid labile group and other substituents are changed. The flow rate does not depend on the percent and type of substitution. Blending two or more distinct polymers brings little change of the flow rate. Through these investigations, it was found that only the flow initiation temperature, that is, the temperature at which the contact hole size becomes reduced changes with the base resin and depends on the glass transition temperature (T_g) of the base resin.

[0016] A summary of these findings can be illustrated in the graph of FIG. 2. In FIG. 2, curve I denotes a low molecular weight polymer, curve II denotes polymer A, curve III denotes polymer B, curve IV denotes a blend of polymer A and polymer B, curve V denotes a polymer having crosslinking groups, curve VI denotes a high molecular weight polymer, and curve VII denotes a polymer having a high T_g. The gradient of the curve represents the flow rate.

[0017] The flow rate can be numerically represented by a change of the contact hole size per degree centigrade of the heating temperature (unit: nm/°C). While the base resin was changed among a variety of polymers, the flow rate did not substantially change. The change of contact hole size per degree centigrade was approximately 20 nm/°C. In the fabrication of LSI devices of the next generation targeting further miniaturization, the flow rate of 20 nm/°C is difficult to control, inadequate to process adaptability, and by no means permissible.

[0018] Based on the above findings, the inventor made further investigations to find that when a contact hole pattern is formed by the thermal flow process using a chemically amplified positive resist composition comprising a compound containing at least two functional groups of the general formula (1) in a molecule, there are achieved a reduced flow rate, improved process control and practical utility.

[0019] By adding a compound containing at least two functional groups of the general formula (1) in a molecule to a chemically amplified positive resist composition, the flow rate in the thermal flow process, that is, the change of

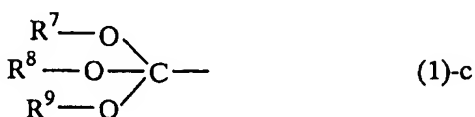
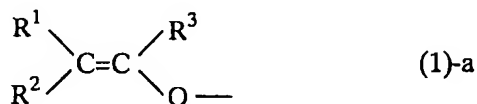
contact hole size per degree centigrade of heating temperature is improved as demonstrated in the graph of FIG. 3. In FIG. 3, curve A denotes a composition having the relevant compound added thereto and curve B denotes a control composition (free of the relevant compound).

[0020] When the compound containing at least two functional groups of the general formula (1) in a molecule is formulated together with a base resin in a chemically amplified positive resist composition, thermal crosslinking reaction can take place between the functional groups and the base resin. This thermal crosslinking reaction proceeds at the heat treating temperature during the thermal flow process, interfering with the rate at which the resist film is fluidized and thereby reducing the flow rate of contact holes. It is believed that the thermal crosslinking reaction of the compound containing at least two functional groups proceeds predominantly with phenolic hydroxyl groups on the base resin, but to some extent, with other sites on the base resin.

[0021] After a chemically amplified positive resist composition having the compound containing at least two functional groups of the general formula (1) in a molecule added thereto was used to form a resist film, which was provided with contact holes and subjected to the thermal flow process, the resulting contact hole pattern configuration was observed. The contact hole pattern was improved in perpendicularity as compared with a control resist composition (without the compound containing at least two functional groups) yielding a contact hole pattern having rounded sidewalls at the end of thermal flow.

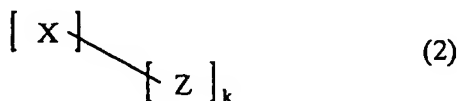
[0022] In summary, it has been found that the addition of the compound containing at least two functional groups of the general formula (1) is effective for reducing the flow rate associated with the thermal flow process of forming a microsize contact hole pattern and that the composition is effectively controllable and process adaptable in the fabrication of LSI devices of the next generation targeting further miniaturization.

[0023] Accordingly, the invention in a first aspect provides a chemically amplified positive resist composition for forming a contact hole pattern by the thermal flow process, comprising a compound containing at least two functional groups of the general formulas (1)-a to (1)-c in a molecule.



[0024] Herein R^1 to R^4 are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, R^5 to R^9 are independently straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, and a pair of R^1 and R^3 , a pair of R^4 and R^5 , a pair of R^5 and R^6 , a pair of R^7 and R^8 , a pair of R^7 and R^9 or a pair of R^8 and R^9 , taken together, may form a ring.

[0025] In one preferred embodiment, the compound containing at least two functional groups is of the general formula (2).

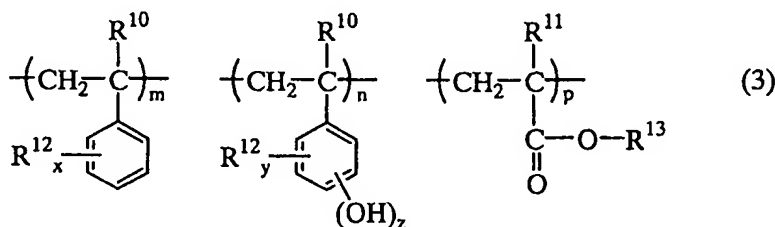


Herein Z is a functional group selected from the formulas (1)-a to (1)-c, the Z's may be the same or different, k is a positive integer of 2 to 6, and X is a k-valent organic group of 2 to 20 carbon atoms.

[0026] Typically the compound of the general formula (2) is present in an amount of 0.1 to 5% by mass of the overall resist composition.

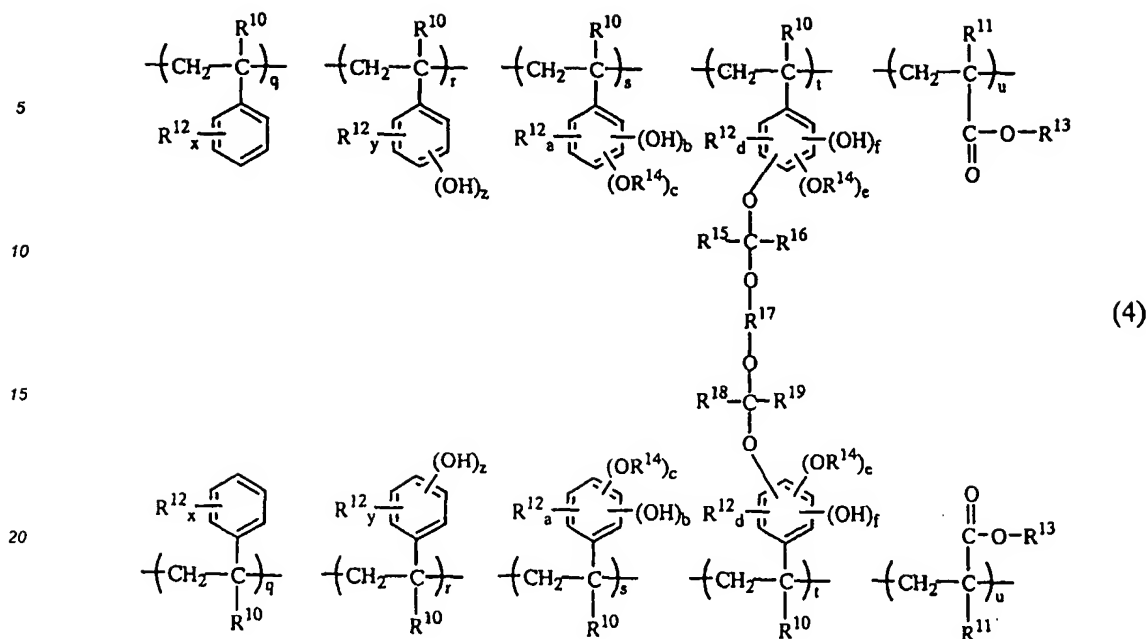
[0027] In a second aspect, the invention provides a chemically amplified positive resist composition for forming a contact hole pattern by the thermal flow process, comprising (A) an organic solvent, (B) a base resin in the form of a polymer having acid labile groups, (C) a photoacid generator, (D) a basic compound, and (E) a compound containing at least two functional groups of the general formulas (1)-a to (1)-c in a molecule, as set forth above.

[0028] In one preferred embodiment, the base resin (B) is a polymer comprising recurring units of the following general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and some of the hydrogen atoms of the remaining phenolic hydroxyl groups are optionally eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in the formula (3). The polymer has a weight average molecular weight of 1,000 to 500,000.



Herein R^{10} is hydrogen or methyl, R^{11} is hydrogen or a methyl, phenyl or cyano group, R^{12} is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms, R^{13} is hydrogen or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, x is 0 or a positive integer of up to 5, y and z are positive integers satisfying $y+z \leq 5$, m and p are 0 or positive numbers, n is a positive number, satisfying $0 \leq m/(m+n+p) \leq 0.8$, $0 < n/(m+n+p) \leq 1$, and $0 \leq p/(m+n+p) \leq 0.8$.

[0029] In a further preferred embodiment, the base resin (B) is a polymer represented by the following general formula (4), that is a polymer comprising recurring units of the general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and some of the hydrogen atoms of the remaining phenolic hydroxyl groups are optionally eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in formula (3). The polymer has a weight average molecular weight of 1,000 to 500,000.



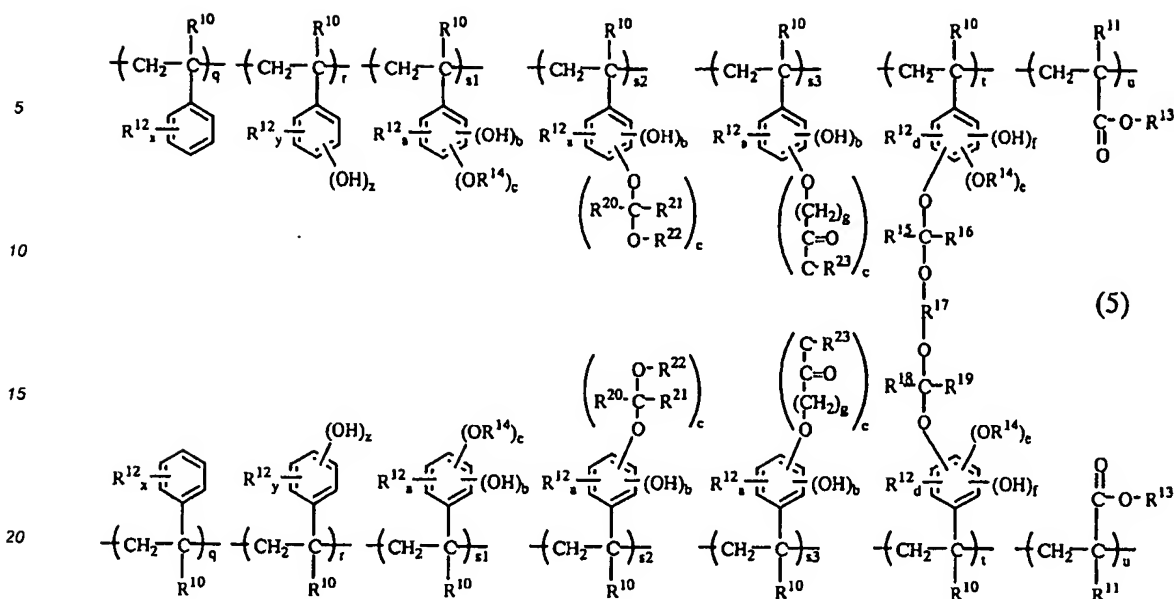
Herein R^{10} is hydrogen or methyl, R^{11} is hydrogen or a methyl, phenyl or cyano group, R^{12} is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms, R^{13} is hydrogen or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, R^{14} is an acid labile group of at least one type, R^{15} , R^{16} , R^{18} and R^{19} are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 6 carbon atoms, and R^{17} is a divalent or polyvalent hydrocarbon group of 1 to 10 carbon atoms which may be separated by an oxygen atom,

each said unit may be constructed of one type or at least two types,

x is 0 or a positive integer of up to 5, y and z are positive integers satisfying $y+z \leq 5$, a , b and c are positive integers satisfying $a+b+c \leq 5$, with the proviso that c is not equal to 0, d , e and f are 0 or positive integers satisfying $d+e+f \leq 4$,

q , t and u are 0 or positive numbers, r and s are positive numbers, satisfying $0 \leq q/(q+r+s+t+u) \leq 0.8$, $0 < s/(q+r+s+t+u) \leq 0.8$, $0 \leq t/(q+r+s+t+u) \leq 0.8$, $0 \leq u/(q+r+s+t+u) \leq 0.8$, $0 < (r+s+t)/(q+r+s+t+u) \leq 1$, and $0 < r/(q+r+s+t+u) \leq 0.8$.

[0030] In a further preferred embodiment, the base resin (B) is a polymer represented by the following general formula (5), that is a polymer comprising recurring units of the general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and some of the hydrogen atoms of the remaining phenolic hydroxyl groups are optionally eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in formula (3). The polymer has a weight average molecular weight of 1,000 to 500,000.



Herein R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , x , y , z , a , b , c , d , e , and f are as defined above.

[0031] R^{21} and R^{22} are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 8 carbon atoms, R^{23} is a monovalent hydrocarbon group of 1 to 18 carbon atoms which may have a hetero atom, a pair of R^{21} and R^{22} , a pair of R^{21} and R^{23} or a pair of R^{22} and R^{23} , taken together, may form a ring, each of R^{21} , R^{22} and R^{23} is a straight or branched alkylene group of 1 to 8 carbon atom when they form a ring, R^{24} is a tertiary alkyl group of 4 to 20 carbon atoms.

g is 0 or a positive integer of 1 to 6, q , s_1 , s_2 , s_3 , t and u are 0 or positive numbers, r is a positive number, satisfying $0 \leq q/(q+r+s_1+s_2+s_3+t+u) \leq 0.8$, $0 \leq s_1/(q+r+s_1+s_2+s_3+t+u) \leq 0.8$, $0 \leq s_2/(q+r+s_1+s_2+s_3+t+u) \leq 0.8$, $0 \leq s_3/(q+r+s_1+s_2+s_3+t+u) \leq 0.8$, $0 < t/(q+r+s_1+s_2+s_3+t+u) \leq 0.8$, $0 < u/(q+r+s_1+s_2+s_3+t+u) \leq 0.8$, $0 < (r+s_1+s_2+s_3+t)/(q+r+s_1+s_2+s_3+t+u) \leq 1$, and $0 < r/(q+r+s_1+s_2+s_3+t+u) \leq 0.8$.

[0032] In the preferred resist composition, component (C) is an onium salt and/or diazomethane derivative; and component (D) is an aliphatic amine.

[0033] In a third aspect, the invention provides a method for forming a contact hole pattern, comprising the steps of (i) applying the chemically amplified positive resist composition of any one of claims 1 to 9 onto a substrate to form a coating, (ii) heat treating the coating and exposing the coating to high energy radiation with a wavelength of up to 300 nm or electron beam through a photo-mask, (iii) optionally heat treating the exposed coating, and developing the coating with a developer, thereby forming a contact hole pattern, and (iv) further heat treating the contact hole pattern for reducing the size of contact holes.

BRIEF DESCRIPTION OF THE DRAWINGS

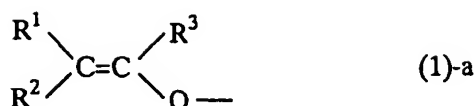
[0034] FIG. 1 illustrates in cross section a contact hole having bowed sidewalls after thermal flow.

[0035] FIG. 2 is a graph showing a contact hole size versus a heating temperature in the thermal flow process.

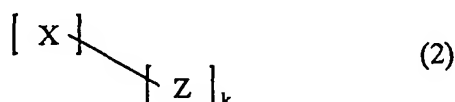
[0036] FIG. 3 is a graph showing the thermal flow rate of a resist composition having added thereto a compound having at least two functional groups and a control composition.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0037] The chemical amplification type, positive working resist composition of the invention comprises a compound containing at least two functional groups of the following general formulas (1)-a to (1)-c in a molecule. A compound of the following general formula (2) is preferred.

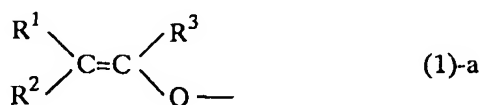


[0038] Herein R¹ to R⁴ are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, R⁵ to R⁹ are independently straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, and a pair of R¹ and R³, a pair of R⁴ and R⁵, a pair of R⁵ and R⁶, a pair of R⁷ and R⁸, a pair of R⁷ and R⁹ or a pair of R⁸ and R⁹, taken together, may form a ring.



[0039] Herein Z is a functional group selected from the formulas (1)-a to (1)-c, the Z's may be the same or different, k is a positive integer of 2 to 6, and X is a k-valent organic group of 2 to 20 carbon atoms.

[0040] Examples of the alkenyloxy group represented by the general formula (1)-a:

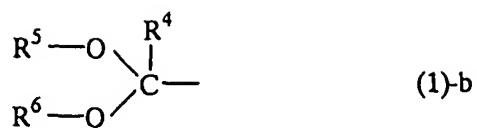


include vinyloxy, propenyloxy, isopropenyloxy and groups of the following formulas.

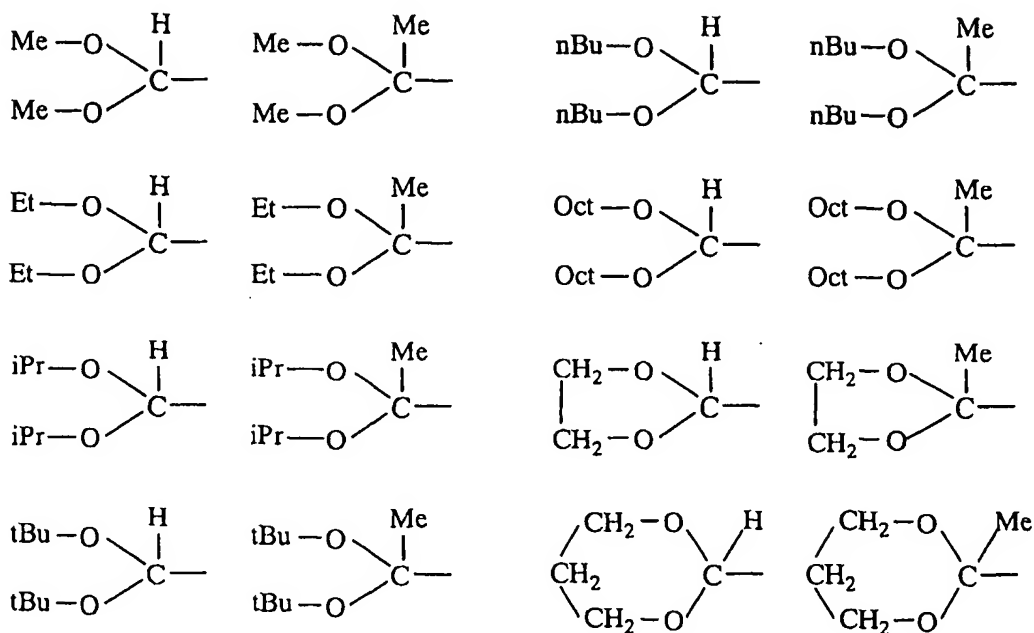


[0041] It is understood that the vinyloxy group is readily obtained by effecting addition reaction of acetylene to a compound having at least two alcohols in its structure (specifically reaction between alcohol and acetylene). The propenyloxy group is readily obtained by reacting an allyl halide with a compound having at least two alcohols in its structure (specifically reaction between alcohol and allyl halide), followed by transition and isomerization of the resulting allyloxy group under basic conditions.

[0042] Examples of the acetal group represented by the general formula (1)-b:



are given below.



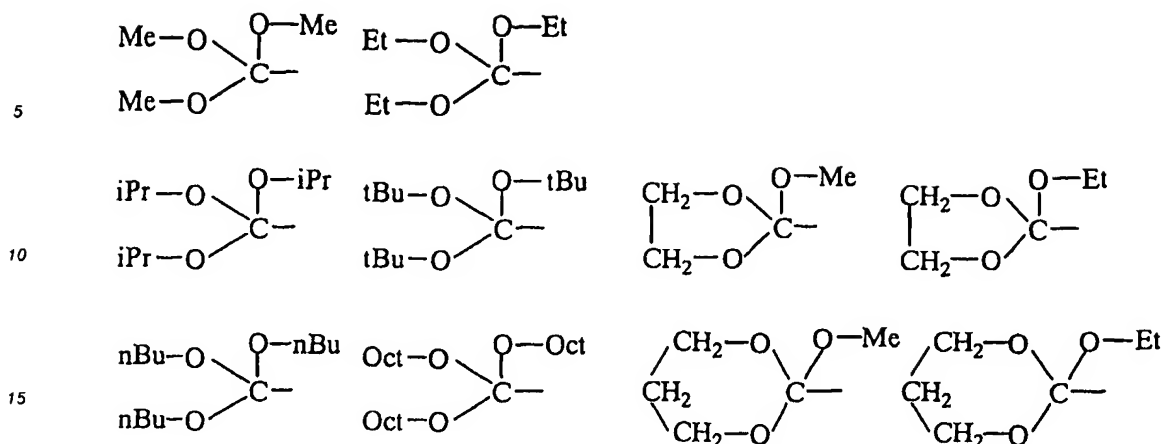
[0043] Herein Me is methyl, Et is ethyl, iPr is isopropyl, nBu is n-butyl, tBu is tert-butyl, and Oct is octyl.

[0044] The acetal group is readily obtained by reacting a compound having at least two aldehyde or ketone groups in its structure with an alcohol under acidic conditions (specifically reaction between aldehyde or ketone and alcohol).

[0045] Examples of the ortho-ester group represented by the general formula (1)-c:



are given below.



[0046] Herein Me is methyl, Et is ethyl, iPr is isopropyl, nBu is n-butyl, tBu is tert-butyl, and Oct is octyl.

[0047] The ortho-ester group is readily obtained by reacting a compound having at least two carboxylate groups in its structure with an alcohol under acidic conditions (specifically reaction between carboxylate and alcohol).

[0048] As described above, the structure of the compound containing functional groups of the formula (1) is represented by the formula (2).

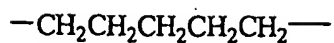
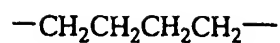


[0049] Herein X is a k-valent organic group of 2 to 20 carbon atoms. The letter k representative of the number of functional groups is a positive integer of 2 to 6.

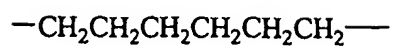
[0050] More particularly, X is selected from substituted or unsubstituted, aliphatic, alicyclic or aromatic hydrocarbon groups of 2 to 20 carbon atoms, which may be separated by a hetero atom such as oxygen, and substituted ones of the foregoing hydrocarbon groups in which some or all of the hydrogen atoms are replaced by halogen atoms such as F, Cl and Br, hydroxyl groups, alkoxy groups, and the like. X has a valence corresponding to the number of Z groups. Where k = 2, for example, X is a substituted or unsubstituted, straight, branched or cyclic alkylene group, arylene group, or aralkylene group, which may be separated by a hetero atom such as oxygen.

[0051] The structure of X is exemplified below.

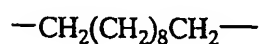
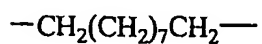
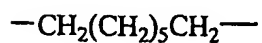
[0052] Where the functional groups are alkenyloxy groups, the difunctional structure is exemplified by ethylene, propylene, isopropylene and the following formulas.



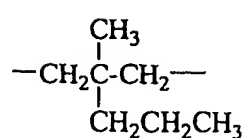
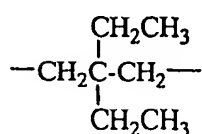
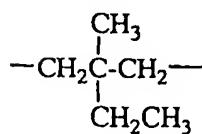
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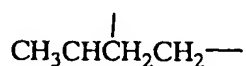
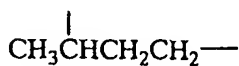
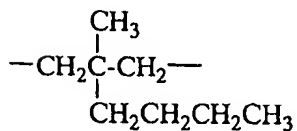
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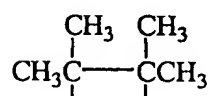
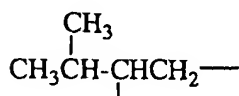
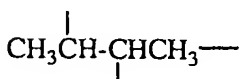
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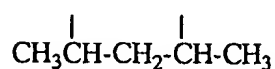
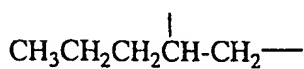
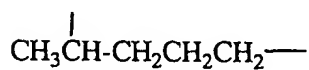
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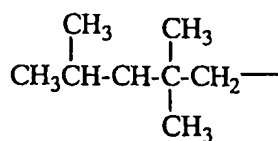
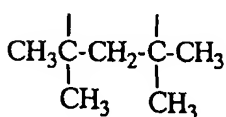
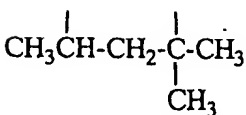
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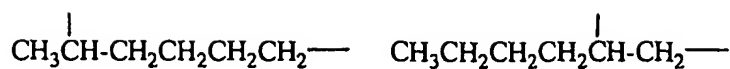
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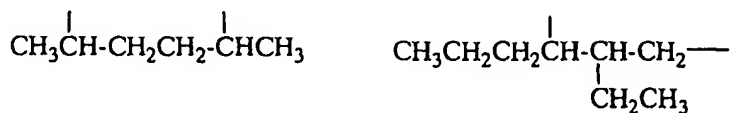
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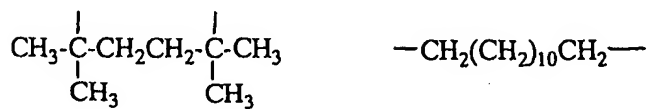
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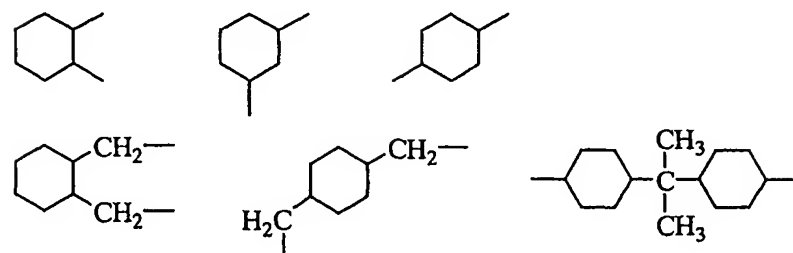
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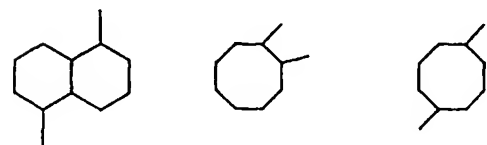
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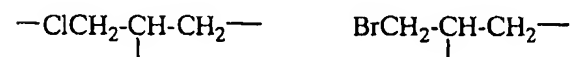
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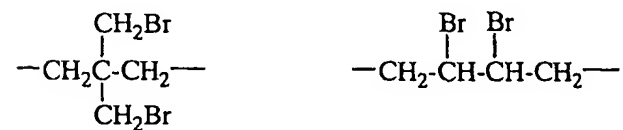
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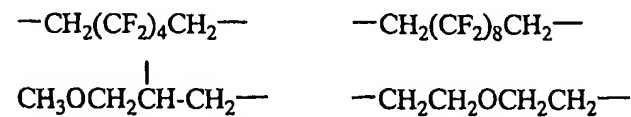
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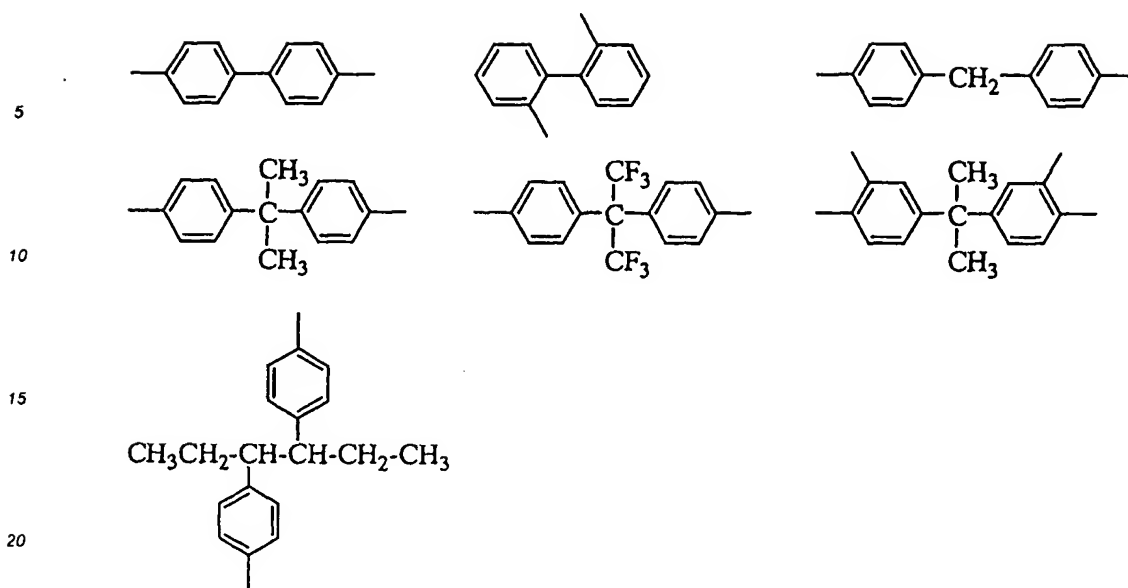


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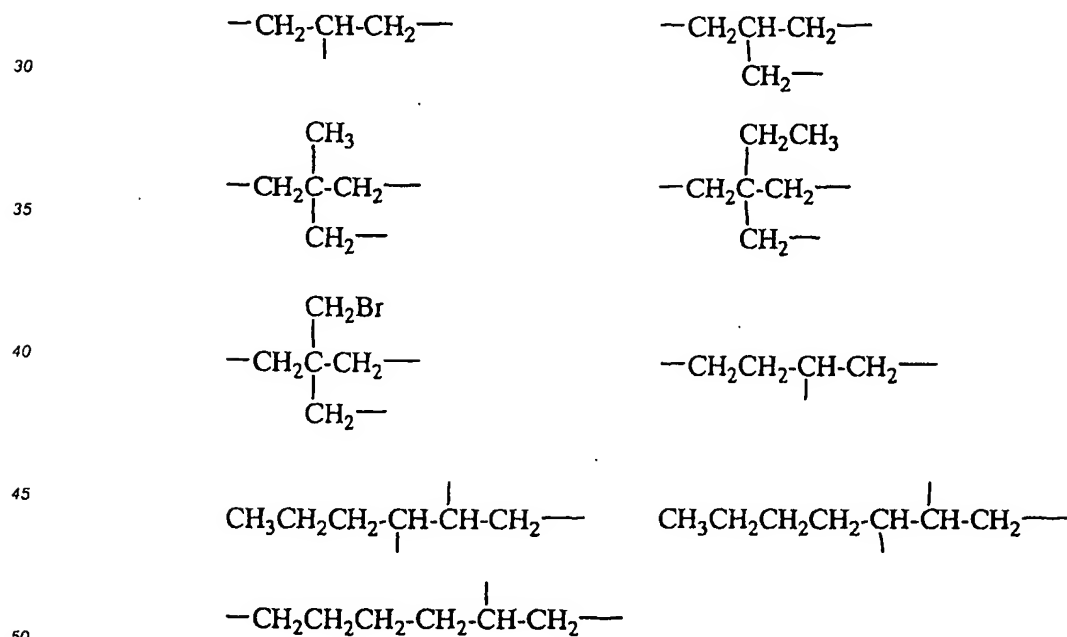


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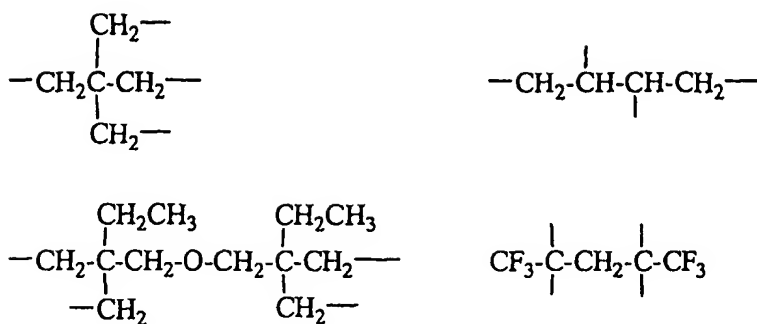


[0053] Where the functional groups are alkenyloxy groups, the trifunctional structure is exemplified by the following formulas.

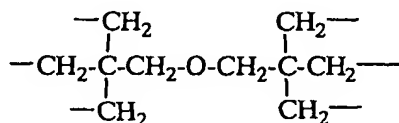


[0054] Where the functional groups are alkenyloxy groups, the tetrafunctional structure is exemplified by the following formulas.

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[0055] Where the functional groups are alkenyloxy groups, the hexafunctional structure is exemplified by the following formula.



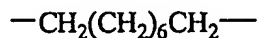
[0056] As described above, the vinyloxy group is readily obtained by effecting addition reaction of acetylene to a compound having at least two alcohols in its structure (specifically reaction between alcohol and acetylene). The propenyloxy group is readily obtained by reacting an allyl halide with a compound having at least two alcohols in its structure (specifically reaction between alcohol and allyl halide), followed by transition and isomerization of the resulting allyloxy group under basic conditions. Where the structure is trifunctional or more, all the alcohol groups may be reacted. There is a situation where two or more alcohols groups are reacted, but alcohol groups are left in the structure. The resulting structure is effective because thermal crosslinking reaction can take place.

[0057] In the case of tetra or more functionality, the polyhydric alcohols which can be used include the examples described below, and they may be reacted with acetylene or allyl halide to form a compound having two or more alkenyloxy groups. Useful polyhydric alcohols include threitol, adonitol, arabitol, xylitol, sorbitol, mannitol, iditol, dulcitol, fucose, ribose, arabinose, xylose, sorbose, mannose, galactose, glucose, and isomers thereof. All alcohol groups in the polyhydric alcohol compound may be substituted with alkenyloxy groups. Alternatively, two or more alcohol groups are substituted with alkenyloxy groups. It is also acceptable that some alcohol groups be substituted with other groups.

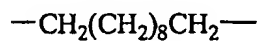
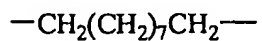
[0058] Where the functional groups are acetal groups, the structure represented by X is exemplified by ethylene, propylene, isopropylene and the following formulas.



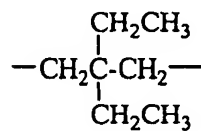
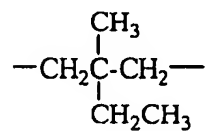
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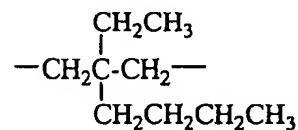
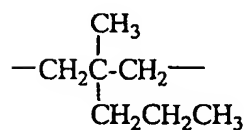
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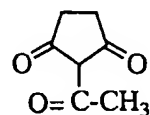
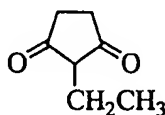
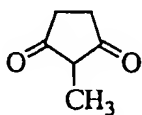
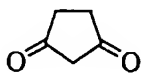
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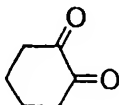
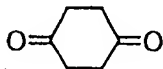
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[0059] As described above, the acetal group is readily obtained by reacting an alcohol with a compound having at least two aldehyde or ketone groups in its structure under acidic conditions (specifically reaction between aldehyde or ketone and alcohol). Use may be made of compounds having at least two acetal groups which are synthesized by reacting compounds having aldehyde or ketone groups as shown below.

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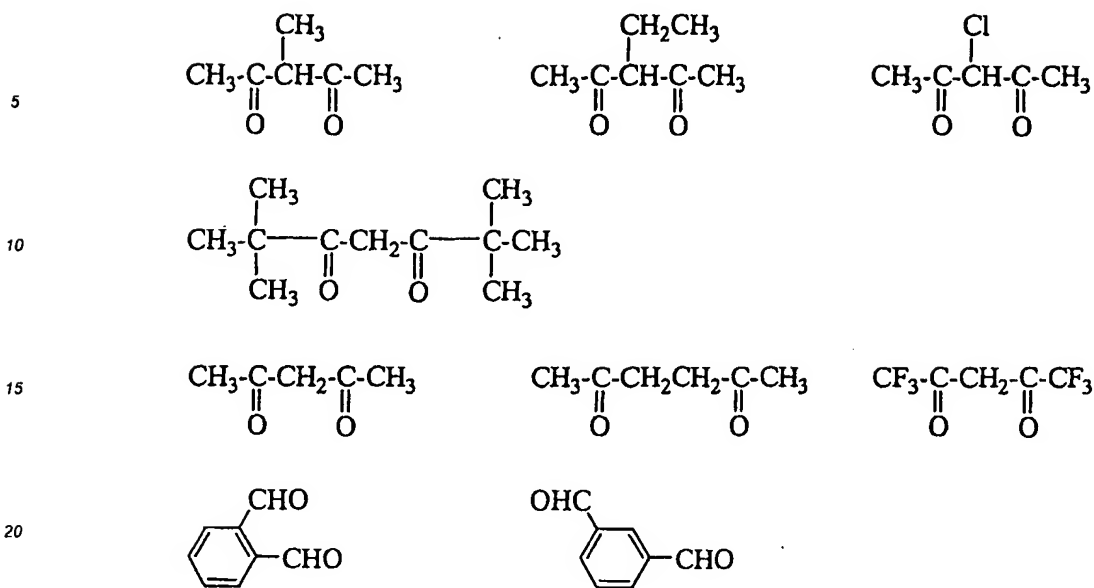


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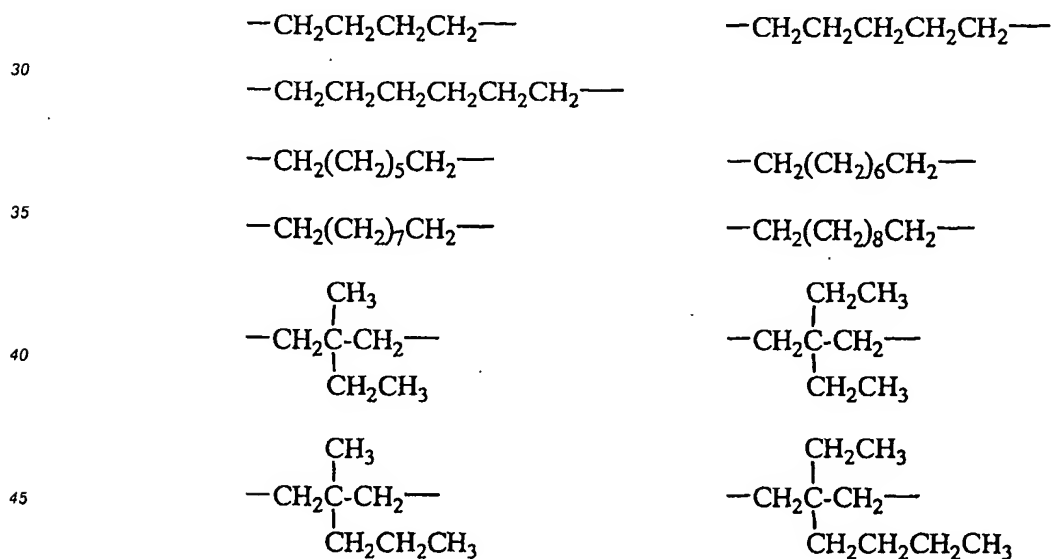
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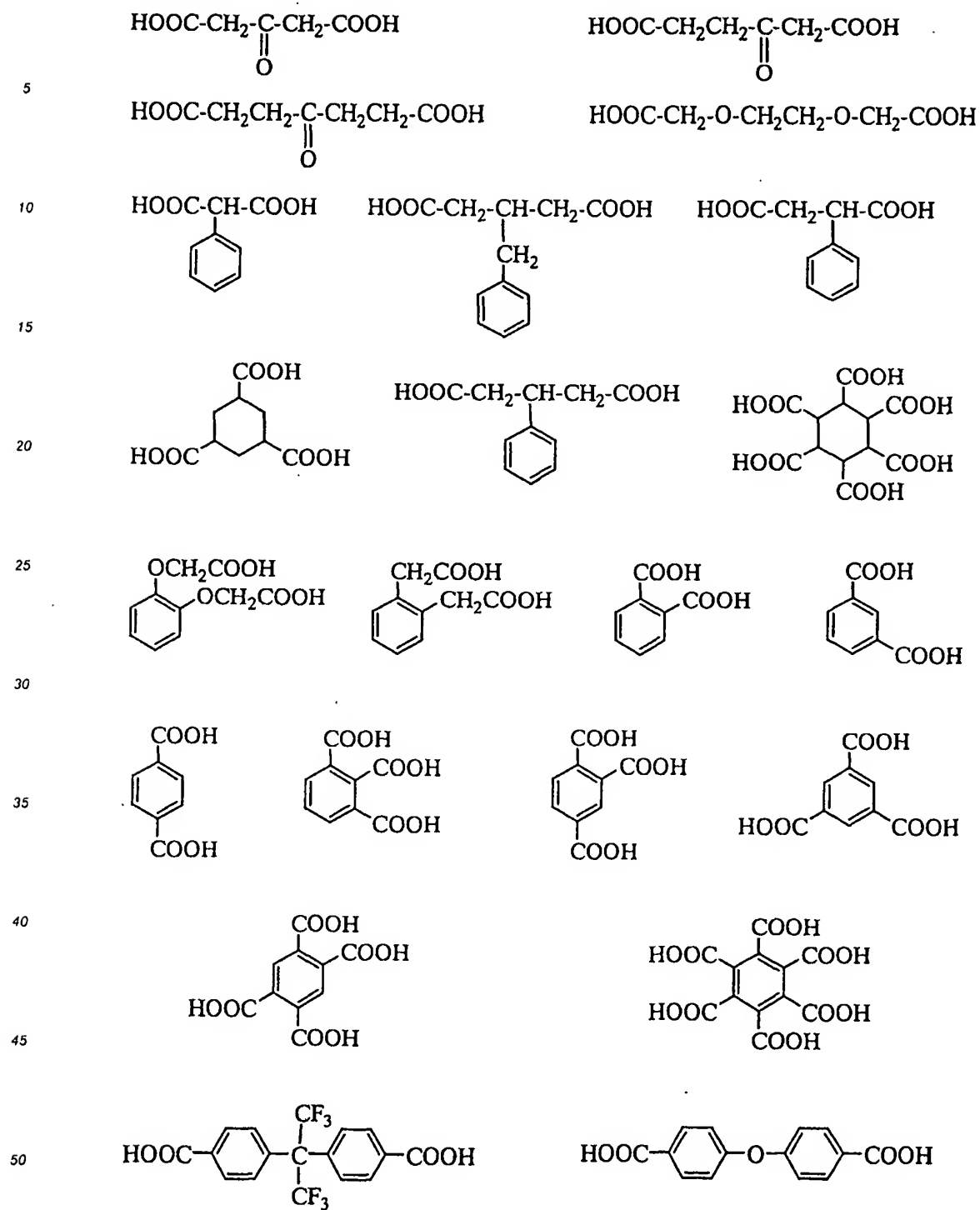


25 [0060] Where the functional groups are ortho-ester groups, the structure represented by X is exemplified by ethylene, propylene, isopropylene and the following formulas.



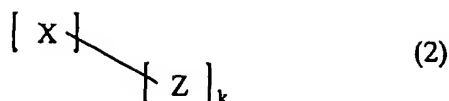
50 [0061] As described above, the ortho-ester group is readily obtained by reacting a compound having at least two carboxylate groups in its structure with an alcohol under acidic conditions (specifically reaction between carboxylate and alcohol). Use may be made of compounds having at least two ortho-ester groups which are synthesized by reacting alcohols with carboxylic ester derivatives as shown below.

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[0062] Where k in the general formula (2):

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is a large number, substantial thermal crosslinking reaction takes place during heat treatment of the thermal flow process or during the baking step after coating of the resist composition, leaving a possibility that scum (or insoluble matter) be left on the resist pattern. Where k is a very small number, thermal crosslinking reaction takes place to a less than desired extent during the thermal flow process so that the flow rate may not be reduced. For this reason, k representative of the number of functional groups in formula (2) is preferably from 2 to 6, and especially from 3 to 4.

[0063] Since an aryl type hydrocarbon has a benzene ring or unsaturated cyclic structure, it absorbs deep UV used with chemically amplified positive resist compositions, typically KrF excimer laser light, leaving the risk of reducing the transmittance of the resist. With a lowering of the resist transmittance, the pattern configuration of contact holes can be exacerbated. For this reason, the structure represented by X favors a saturated hydrocarbon rather than the aryl type hydrocarbon.

[0064] Z represents a functional group of the general formula (1) and may be the same or a mixture of different functional groups.

[0065] The compound having at least two functional groups of the general formula (1) is preferably added to a chemically amplified positive resist composition in an amount of 0.1 to 5% by mass based on the entire resist composition. Outside the range, a less amount of the compound may be less effective for controlling the thermal flow rate whereas a larger amount of the compound may cause scum generation probably due to abnormal thermal crosslinking and adversely affect the resist sensitivity. A more appropriate amount is 0.5 to 2% by mass of the compound.

[0066] On use, the compound having at least two functional groups of the general formula (1) is added to a chemically amplified positive resist composition. Where the compound has a relatively low boiling point, there would arise a problem that if the resist coated on a substrate is held for some time prior to exposure, the compound in the resist coating will volatilize in that duration whereby the sensitivity of contact hole formation and the size of contact holes are altered. This problem is generally known as post coating delay and should be avoided in the device fabrication. For this reason, the compound should preferably have a relatively high boiling point so that it will not volatilize during the holding of the resist-coated substrate. Most preferably, the compound has a boiling point in excess of 200°C under atmospheric pressure.

[0067] In addition to the compound having at least two functional groups of the general formula (1), the chemically amplified positive resist composition for forming a contact hole pattern according to the invention typically contains:

- (A) an organic solvent,
- (B) a base resin in the form of a polymer having acid labile groups,
- (C) a photoacid generator, and
- (D) a basic compound.

40 (A) Organic solvent

[0068] The organic solvent used herein may be any organic solvent in which the base resin, photoacid generator, dissolution regulator, and other components are soluble. Illustrative, non-limiting, examples of the organic solvent include ketones such as cyclohexanone and methyl-2-n-amylketone; alcohols such as 3-methoxybutanol, 3-methyl-3-methoxybutanol, 1-methoxy-2-propanol, and 1-ethoxy-2-propanol; ethers such as propylene glycol monomethyl ether, ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol dimethyl ether, and diethylene glycol dimethyl ether; and esters such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, ethyl lactate, ethyl pyruvate, butyl acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, tert-butyl acetate, tert-butyl propionate, and propylene glycol mono-tert-butyl ether acetate. These solvents may be used alone or in combinations of two or more thereof. Of the above organic solvents, it is recommended to use diethylene glycol dimethyl ether, 1-ethoxy-2-propanol and ethyl lactate because the photoacid generator serving as one of the resist components is most soluble therein, propylene glycol monomethyl ether acetate because it is a safe solvent, or a mixture thereof.

[0069] An appropriate amount of the organic solvent used is about 200 to 1,000 parts, especially about 400 to 800 parts by mass per 100 parts by mass of the base resin.

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(B) Base resin

[0070] An appropriate base resin used herein is a resin which changes its solubility in an alkaline developer solution under the action of an acid. It is typically, though not limited thereto, an alkali-soluble resin having phenolic hydroxyl and/or carboxyl groups in which some or all of the phenolic hydroxyl and/or carboxyl groups are protected with acid-labile protective groups having C-O-C.

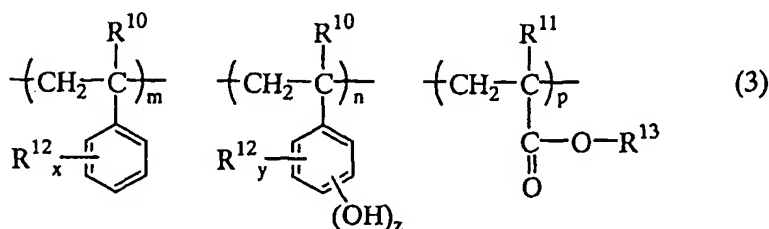
[0071] The alkali-soluble resins having phenolic hydroxyl and/or carboxyl groups include homopolymers and copolymers of p-hydroxystyrene, m-hydroxystyrene, α -methyl-p-hydroxystyrene, 4-hydroxy-2-methylstyrene, 4-hydroxy-3-methylstyrene, methacrylic acid and acrylic acid, and such copolymers having a carboxylic derivative or diphenyl ethylene introduced at their terminus.

[0072] Also included are copolymers in which units free of alkali-soluble sites such as styrene, α -methylstyrene, acrylate, methacrylate, hydrogenated hydroxystyrene, maleic anhydride and maleimide are introduced in addition to the above-described units in such a proportion that the solubility in an alkaline developer may not be extremely reduced. Substituents on the acrylates and methacrylates may be any of the substituents which do not undergo acidolysis. Exemplary substituents are straight, branched or cyclic C₁₋₈ alkyl groups and aromatic groups such as aryl groups, but not limited thereto.

[0073] Examples include poly(p-hydroxystyrene), poly(m-hydroxystyrene), poly(4-hydroxy-2-methylstyrene), poly(4-hydroxy-3-methylstyrene), poly(α -methyl-p-hydroxystyrene), partially hydrogenated p-hydroxystyrene copolymers, p-hydroxystyrene- α -methyl-p-hydroxystyrene copolymers, p-hydroxystyrene- α -methylstyrene copolymers, p-hydroxystyrene-styrene copolymers, p-hydroxystyrene-m-hydroxystyrene copolymers, p-hydroxystyrene-styrene copolymers, p-hydroxystyrene-acrylic acid copolymers, p-hydroxystyrene-methacrylic acid copolymers, p-hydroxystyrene-methyl methacrylate copolymers, p-hydroxystyrene-acrylic acid-methyl methacrylate copolymers, p-hydroxystyrene-methyl acrylate copolymers, p-hydroxystyrene-methacrylic acid-methyl methacrylate copolymers, poly(methacrylic acid), poly(acrylic acid), acrylic acid-methyl acrylate copolymers, methacrylic acid-methyl methacrylate copolymers, acrylic acid-maleimide copolymers, methacrylic acid-maleimide copolymers, p-hydroxystyrene-acrylic acid-maleimide copolymers, and p-hydroxystyrene-methacrylic acid-maleimide copolymers, but are not limited to these combinations.

[0074] Preferred are poly(p-hydroxystyrene), partially hydrogenated p-hydroxystyrene copolymers, p-hydroxystyrene-styrene copolymers, p-hydroxystyrene-acrylic acid copolymers, and p-hydroxystyrene-methacrylic acid copolymers.

[0075] The preferred base resin is an alkali-soluble resin comprising recurring units of the following general formula (3). The preferred base resin is a polymer comprising recurring units of the general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and/or some of the hydrogen atoms of the remaining phenolic hydroxyl groups are eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in the formula (3). The polymer has a weight average molecular weight of 1,000 to 500,000,



[0076] In formula (3), R¹⁰ is hydrogen or methyl, R¹¹ is hydrogen or a methyl, phenyl or cyano group, R¹² is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms, R¹³ is hydrogen or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, x is 0 or a positive integer of up to 5, y and z are positive integers satisfying y+z ≤ 5, m and p are 0 or positive numbers, n is a positive number, satisfying 0 ≤ m/(m+n+p) ≤ 0.8, 0 < n/(m+n+p) ≤ 1, and 0 ≤ p/(m+n+p) ≤ 0.8.

[0077] The polymer should have a weight average molecular weight (Mw) of 1,000 to 500,000, and especially 3,000 to 100,000. With a Mw of less than 1,000, polymers would perform poorly and often lack heat resistance and film formability. Polymers with a Mw of more than 500,000 would be less soluble in a developer and a resist solvent because of their too high molecular weight. Also the polymer should preferably have a dispersity (Mw/Mn) of up to 3.5, preferably up to 1.5. A dispersity of more than 3.5 often leads to poor resolution.

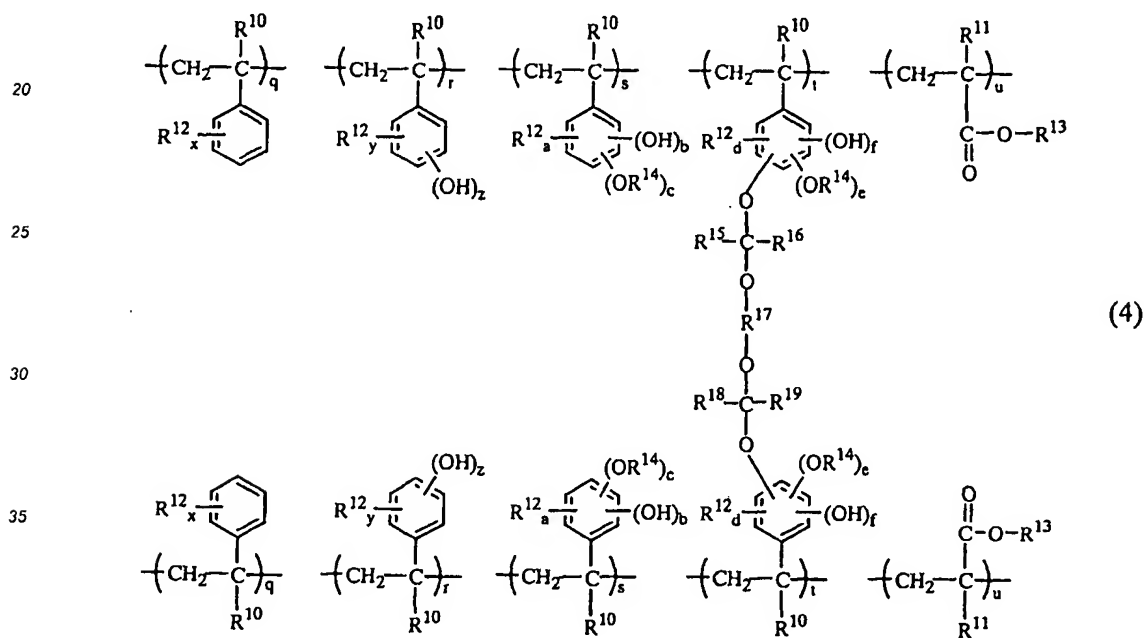
[0078] The preparation method is not critical although poly(p-hydroxystyrene) and similar polymers can be synthe-

sized by living anion polymerization to a low or narrow dispersity.

[0079] More preferably, the base resin (B) is a polymer comprising recurring units of the formula (3), that is, a

[0080] copolymer containing p-hydroxystyrene and/or α -methyl-p-hydroxystyrene and an acrylic acid and/or methacrylic acid in which some hydrogen atoms of phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, the acrylate and/or methacrylate is an ester protected with an acid labile group, the units of acrylate and methacrylate are contained in the polymer in a proportion of more than 0 mol% to 50 mol% on the average, and the acid labile groups are present in a proportion of more than 0 mol% to 80 mol%, on the average, based on the entire polymer.

[0081] This polymer is typically a polymer represented by the following general formula (4), that is a polymer comprising recurring units of the general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and/or some of the hydrogen atoms of the remaining phenolic hydroxyl groups are eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in formula (3). The polymer has a weight average molecular weight of 1,000 to 500,000,

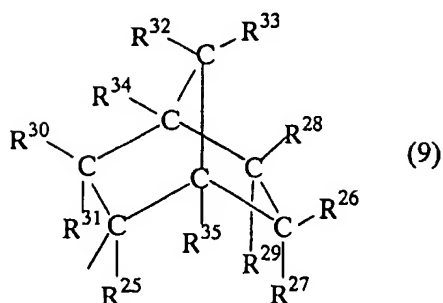
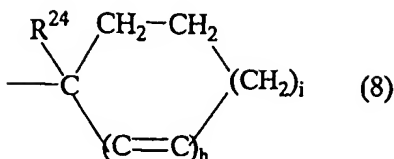
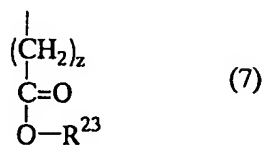
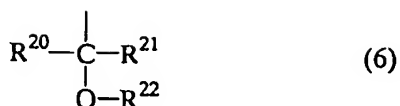


[0082] Herein R^{10} is hydrogen or methyl, R^{11} is hydrogen or a methyl, phenyl or cyano group, R^{12} is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms, R^{13} is hydrogen or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, R^{14} is an acid labile group of at least one type, R^{15} , R^{16} , R^{18} and R^{19} are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 6 carbon atoms, and R^{17} is a divalent or polyvalent hydrocarbon group of 1 to 10 carbon atoms which may be separated by an oxygen atom, for example, a straight, branched or cyclic alkylene, alkylene ether, and arylene such as phenylene. Each unit may be constructed of one type or at least two types.

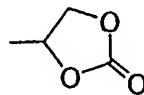
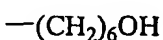
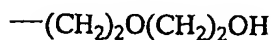
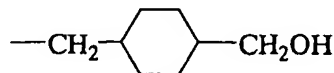
[0083] The letter x is 0 or a positive integer of up to 5, y and z are positive integers satisfying $y+z \leq 5$; a, b and c are positive integers satisfying $a+b+c \leq 5$, with the proviso that c is not equal to 0; d, e and f are 0 or positive integers satisfying $d+e+f \leq 4$; q, l and u are 0 or positive numbers, r and s are positive numbers, satisfying $0 \leq q/(q+r+s+t+u) \leq 0.8$, $0 < s/(q+r+s+t+u) \leq 0.8$, $0 \leq t/(q+r+s+t+u) \leq 0.8$, $0 < u/(q+r+s+t+u) \leq 0.8$, $0 < (r+s+t)/(q+r+s+t+u) \leq 1$, and $0 < r/(q+r+s+t+u) \leq 0.8$.

[0084] Illustrative, non-limiting, examples of the straight, branched or cyclic alkyl groups of 1 to 8 carbon atoms represented by R^{12} include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, cyclohexyl, and cyclopentyl.

[0085] With respect to the acid labile groups represented by R^{14} , where some phenolic hydroxyl groups on the alkali-soluble resin are protected with acid labile substituents having C-O-C linkages, the acid labile groups are selected from a variety of such groups. The preferred acid labile groups are groups of the following general formulae (6) to (9), tertiary alkyl group of 4 to 20 carbon atoms, preferably 4 to 15 carbon atoms, trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms, or oxoalkyl groups of 4 to 20 carbon atoms.



[0086] Herein R^{20} and R^{21} are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, cyclopentyl, cyclohexyl, 2-ethylhexyl and n-octyl. R^{22} is a monovalent hydrocarbon group of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, which may have a hetero atom (e.g., oxygen atom), for example, straight, branched or cyclic alkyl groups, and such groups in which some hydrogen atoms are replaced by hydroxyl, alkoxy, oxo, amino or alkylamino groups. Illustrative examples of the substituted alkyl groups are given below.



[0087] A pair of R^{20} and R^{21} , a pair of R^{20} and R^{22} , or a pair of R^{21} and R^{22} , taken together, may form a ring. Each of R^{20} , R^{21} and R^{22} is a straight or branched alkylene group of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, when they form a ring.

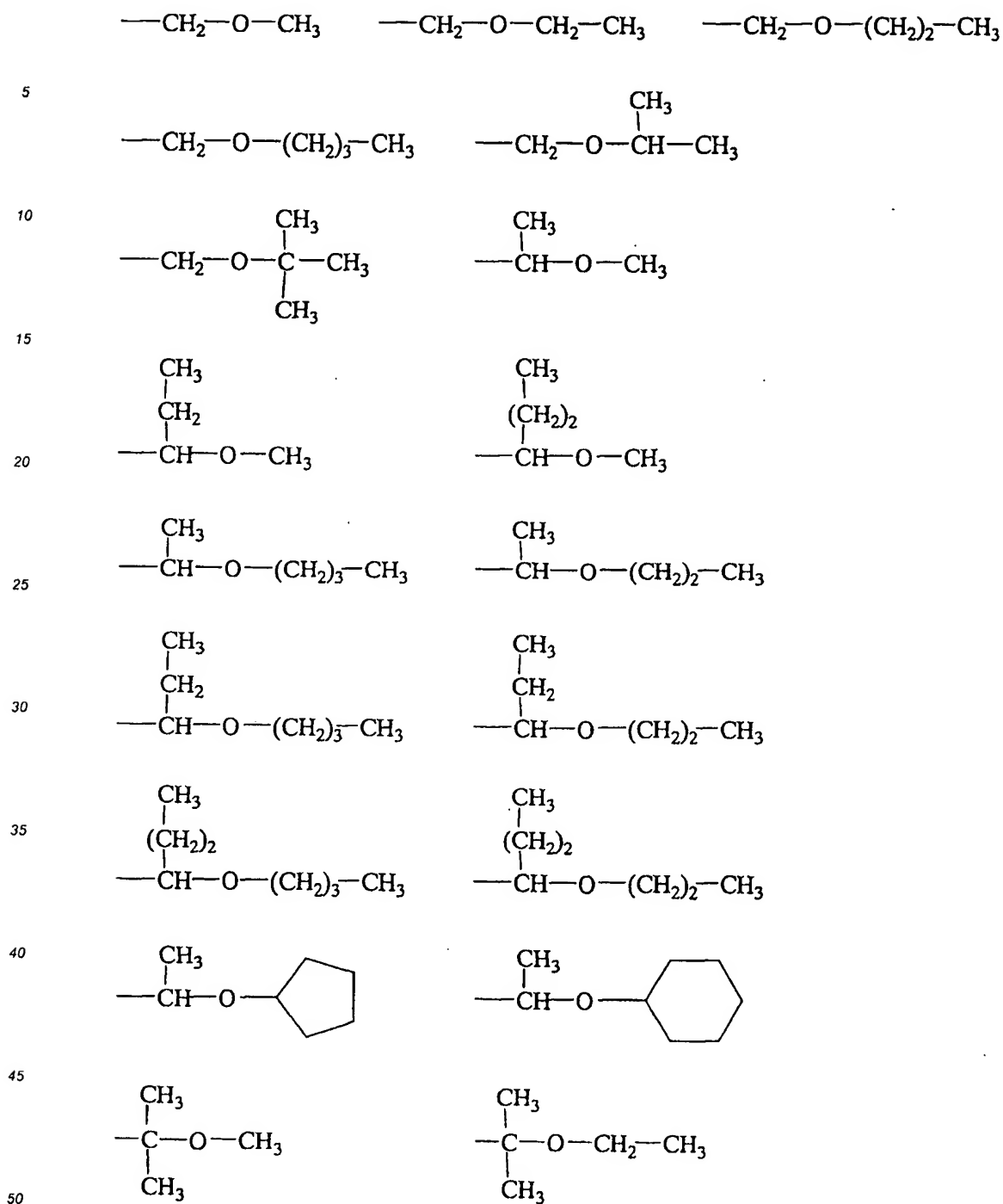
[0088] R^{23} is a tertiary alkyl group of 4 to 20 carbon atoms, preferably 4 to 15 carbon atoms, a trialkylsilyl group whose alkyl groups each have 1 to 6 carbon atoms, an oxoalkyl group of 4 to 20 carbon atoms or a group of formula (6). Exemplary tertiary alkyl groups are tert-butyl, tert-amyl, 1,1-diethylpropyl, 1-ethylcyclopentyl, 1-butylcyclopentyl, 1-ethylcyclohexyl, 1-butylcyclohexyl, 1-ethyl-2-cyclopentenyl, 1-ethyl-2-cyclohexenyl, and 2-methyl-2-adamantyl. Ex-

emplary trialkylsilyl groups are trimethylsilyl, triethylsilyl, and dimethyl-tert-butylsilyl. Exemplary oxoalkyl groups are 3-oxocyclohexyl, 4-methyl-2-oxooxan-4-yl, and 5-methyl-5-oxooxoran-4-yl. Letter z is an integer of 0 to 6.

[0089] R²⁴ is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms or substituted or unsubstituted aryl group of 6 to 20 carbon atoms. Exemplary straight, branched or cyclic alkyl groups include methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, tert-amyl, n-pentyl, n-hexyl, cyclopentyl, cyclohexyl, cyclopentylmethyl, cyclopentylethyl, cyclohexylmethyl and cyclohexylethyl. Exemplary substituted or unsubstituted aryl groups include phenyl, methylphenyl, naphthyl, anthryl, phenanthryl, and pyrenyl. Letter h is equal to 0 or 1, i is equal to 0, 1, 2 or 3, satisfying 2h+i = 2 or 3.

[0090] R²⁵ is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms or substituted or unsubstituted aryl group of 6 to 20 carbon atoms, examples of which are as exemplified for R²⁴. R²⁶ to R³⁵ are independently hydrogen or monovalent hydrocarbon groups of 1 to 15 carbon atoms which may contain a hetero atom, for example, straight, branched or cyclic alkyl groups such as methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, tert-amyl, n-pentyl, n-hexyl, n-octyl, n-nonyl, n-decyl, cyclopentyl, cyclohexyl, cyclopentylmethyl, cyclopentylethyl, cyclopentylbutyl, cyclohexylmethyl, cyclohexylethyl, and cyclohexylbutyl, and substituted ones of these groups in which some hydrogen atoms are replaced by hydroxyl, alkoxy, carboxy, alkoxycarbonyl, oxo, amino, alkylamino, cyano, mercapto, alkylthio, and sulfo groups. R²⁶ to R³⁵, for example, a pair of R²⁶ and R²⁷, a pair of R²⁶ and R²⁸, a pair of R²⁷ and R²⁹, a pair of R²⁸ and R²⁹, a pair of R³⁰ and R³¹, or a pair of R³² and R³³, taken together, may form a ring. When R²⁶ to R³⁶ form a ring, they are divalent C₁-C₁₅ hydrocarbon groups which may contain a hetero atom, examples of which are the above-exemplified monovalent hydrocarbon groups with one hydrogen atom eliminated. Also, two of R²⁶ to R³⁵ which are attached to adjacent carbon atoms (for example, a pair of R²⁶ and R²⁸, a pair of R²⁸ and R³⁴, or a pair of R³² and R³⁴) may directly bond together to form a double bond.

[0091] Of the acid labile groups of formula (6), illustrative examples of the straight or branched groups are given below.

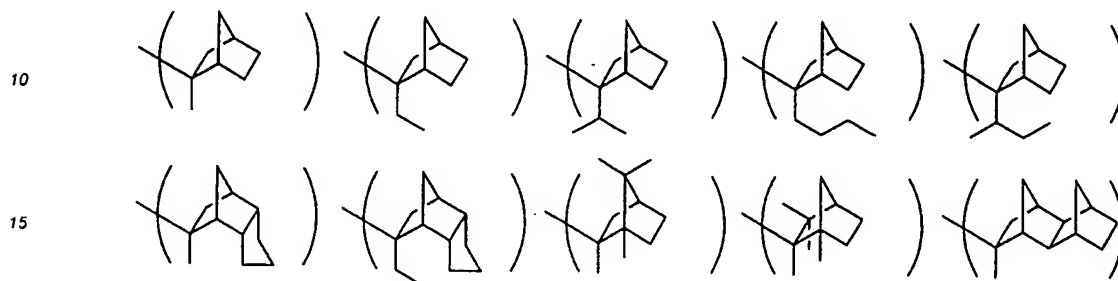


[0092] Of the acid labile groups of formula (6), illustrative examples of the cyclic groups include tetrahydrofuran-2-yl, 2-methyltetrahydrofuran-2-yl, tetrahydropyran-2-yl and 2-methyltetrahydropyran-2-yl.

[0093] Illustrative examples of the acid labile groups of formula (7) include tert-butoxycarbonyl, tert-butoxycarbonylmethyl, tert-amylloxycarbonyl, tert-amylloxycarbonylmethyl, 1,1-diethylpropyloxycarbonyl, 1,1-diethylpropyloxycarbonylmethyl, 1-ethylcyclopentyloxycarbonyl, 1-ethylcyclopentyloxycarbonylmethyl, 1-ethyl-2-cyclopentyloxycarbonyl, 1-ethyl-2-cyclopentyloxycarbonylmethyl, 1-ethoxyethoxy carbonylmethyl, 2-tetrahydropyranyloxycarbonylmethyl, and 2-tetrahydrofuranyloxycarbonylmethyl.

[0094] Illustrative examples of the acid labile groups of formula (8) include 1-methylcyclopentyl, 1-ethylcyclopentyl, 1-n-propylcyclopentyl, 1-isopropylcyclopentyl, 1-n-butylcyclopentyl, 1-sec-butylcyclopentyl, 1-methylcyclohexyl, 1-ethylcyclohexyl, 3-methyl-1-cyclopenten-3-yl, 3-ethyl-1-cyclopenten-3-yl, 3-methyl-1-cyclohexen-3-yl, and 3-ethyl-1-cyclohexen-3-yl.

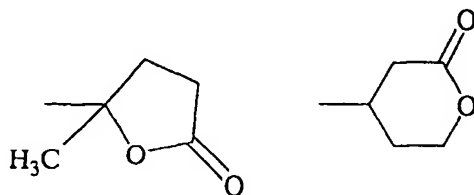
[0095] Illustrative examples of the acid labile groups of formula (9) are given below.



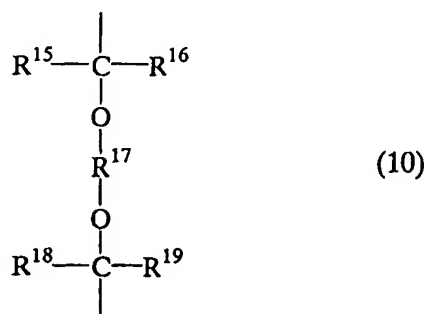
[0096] Exemplary of the tertiary alkyl group of 4 to 20 carbon atoms, preferably 4 to 15 carbon atoms, are tert-butyl, tert-amyl, 3-ethyl-3-pentyl and dimethylbenzyl.

[0097] Exemplary of the trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms are trimethylsilyl, triethylsilyl, and tert-butyl dimethylsilyl.

[0098] Exemplary of the oxoalkyl groups of 4 to 20 carbon atoms are 3-oxocyclohexyl and groups represented by the following formulae.

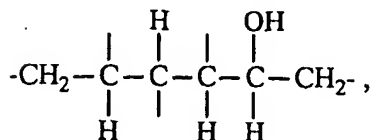
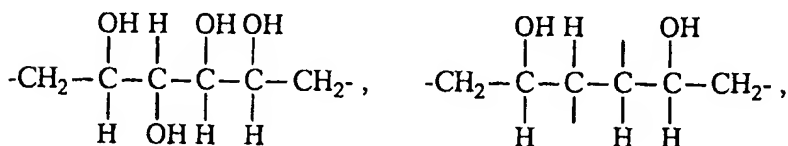
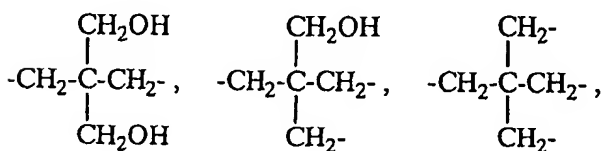
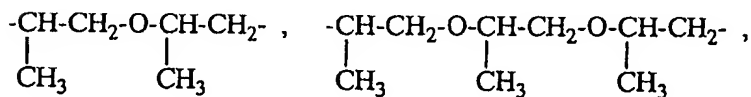
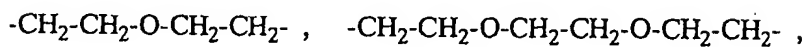
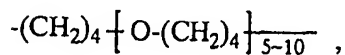
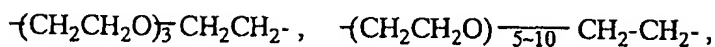
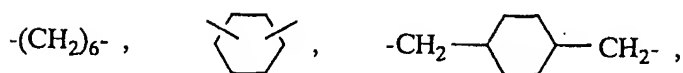
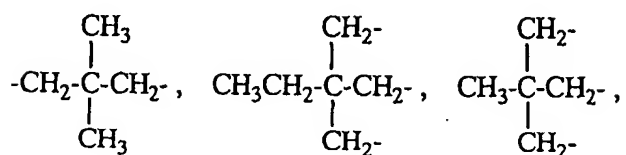
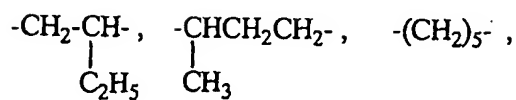
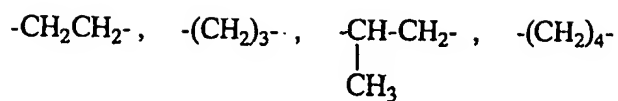


[0099] Also the base resin (B) may be a polymer comprising units of formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of one or more types, and the hydrogen atoms of the remaining phenolic hydroxyl groups are crosslinked within a molecule and/or between molecules, in a proportion of more than 0 mol% to 80 mol%, on the average, of the entire phenolic hydroxyl groups on the polymer of formula (3), with crosslinking groups having C-O-C linkages represented by the following general formula (10).



[0100] Herein, R^{15} , R^{16} , R^{18} and R^{19} are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 6 carbon atoms, examples of which are the same as exemplified for R^{12} . R^{17} is a divalent or more valent straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, alkyl ether, cyclohexyl or aryl group.

[0101] Illustrative examples of R^{17} in formula (10) are given below.



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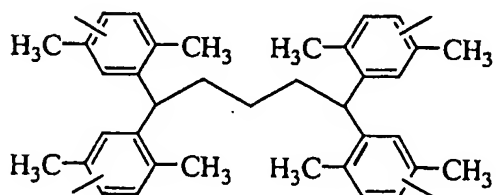
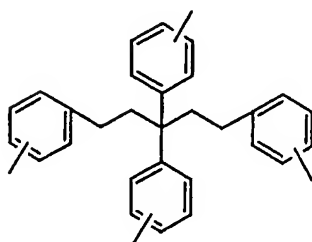
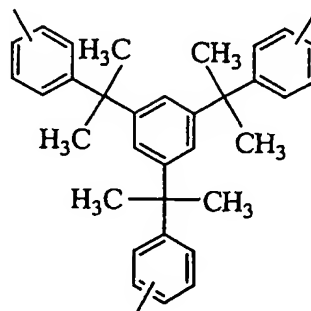
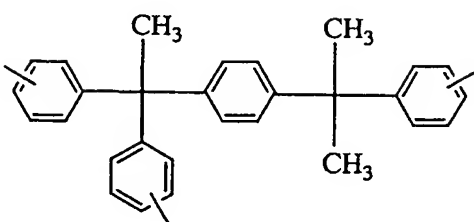
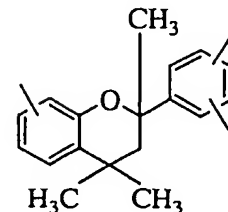
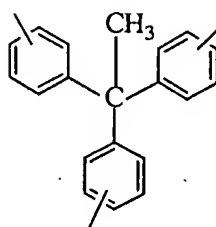
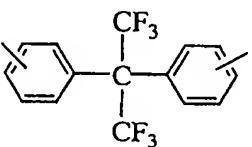
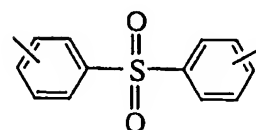
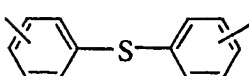
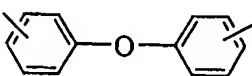
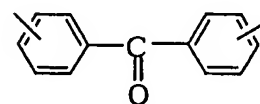
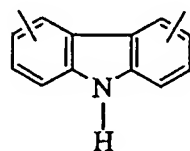
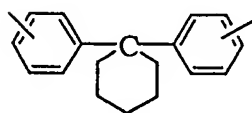
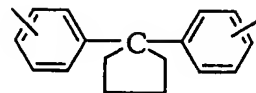
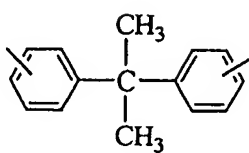
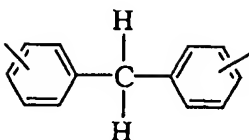
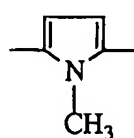
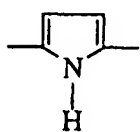
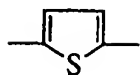
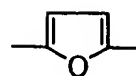
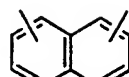
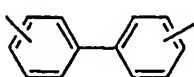
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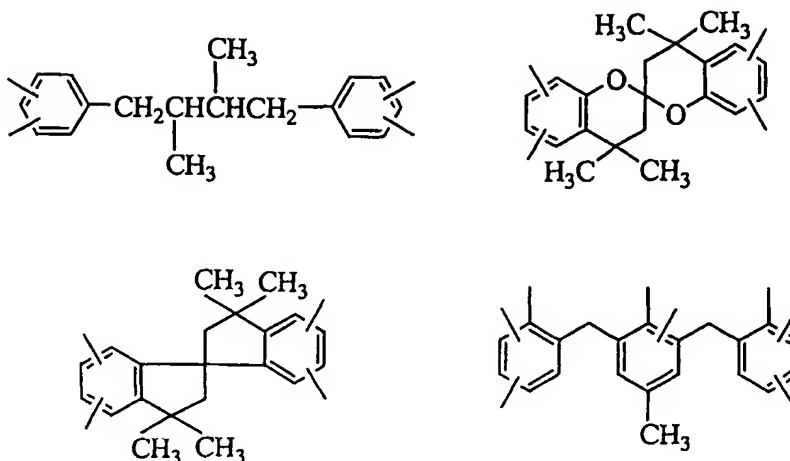
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[0102] These crosslinking groups having C-O-C linkages within and/or between molecules are readily obtainable by reacting phenolic hydroxyl groups with alkenyl ether compounds or halogenated alkyl ether compounds.

[0103] Where the base resin in the resist composition according to the invention is crosslinked with acid labile substituents, it is a polymer which is obtained by reacting phenolic hydroxyl groups with an alkenyl ether compound or halogenated alkyl ether such that the polymer is crosslinked within a molecular and/or between molecules with crosslinking groups having C-O-C linkages, wherein the total amount of the acid labile groups and crosslinking groups is preferably, on the average, more than 0 mol% to 80 mol%, especially 2 to 50 mol%, based on the entire phenolic hydroxyl groups in formula (3).

[0104] An appropriate proportion of crosslinking groups having C-O-C linkages is, on the average, from more than 0 mol% to 50 mol%, and especially from 0.2 to 20 mol%. With 0 mol%, few benefits of the crosslinking group are obtained, resulting in a reduced contrast of alkali dissolution rate and a low resolution. With more than 50 mol%, a too much crosslinked polymer would gel, become insoluble in alkali, induce a film thickness change, internal stresses or bubbles upon alkali development, and lose adhesion to the substrate due to less hydrophilic groups.

[0105] The proportion of acid labile groups is on the average preferably from more than 0 mol% to 80 mol%, especially from 10 to 50 mol%. With 0 mol%, there may result a reduced contrast of alkali dissolution rate and a low resolution. With more than 80 mol%, there may result a loss of alkali dissolution, less affinity to an alkali developer upon development, and a low resolution.

[0106] By properly selecting the proportions of crosslinking groups having C-O-C linkages and acid labile groups within the above-defined ranges, it becomes possible to control the size and configuration of a resist pattern as desired. The contents of crosslinking groups having C-O-C linkages and acid labile groups in the polymer have substantial influence on the dissolution rate contrast of a resist film and govern the properties of the resist composition relating to the size and configuration of a resist pattern.

[0107] In the resist composition, the preferred acid labile groups introduced in the base resin (B) are 1-ethoxycyclopentyl, 1-ethoxycyclohexylcarbonylmethyl, tert-amyl, 1-ethoxyethyl, 1-ethoxypropyl, tetrahydrofuranyl, tetrahydropyranyl, tert-butyl, 1-ethylcyclohexyl, tert-butoxycarbonyl, tert-butoxycarbonylmethyl groups, and substituents of formula (10) wherein R¹⁵ and R¹⁸ are methyl, R¹⁶ and R¹⁹ are hydrogen, and R¹⁷ is ethylene, 1,4-butylene or 1,4-cyclohexylene.

[0108] In a single polymer, these substituents may be incorporated alone or in admixture of two or more types. A blend of two or more polymers having substituents of different types is also acceptable.

[0109] Appropriate combinations of substituents of two or more types include a combination of acetal with acetal analog, a combination of acetal with a substituent having a different degree of scission by acid such as tert-butoxy, a combination of a crosslinking acid labile group with acetal, and a combination of a crosslinking acid labile group with a substituent having a different degree of scission by acid such as tert-butoxy.

[0110] The percent proportion of these substituents substituting for phenol and carboxyl groups in the polymer is not critical. Preferably the percent substitution is selected such that when a resist composition comprising the polymer is applied onto a substrate to form a coating, the unexposed area of the coating may have a dissolution rate of 0.01 to 10 /Å sec in a 2.38% tetramethylammonium hydroxide (TMAH) developer.

[0111] On use of a polymer containing a greater proportion of carboxyl groups which can reduce the alkali dissolution rate, the percent substitution must be increased or non-acid-labile substituents to be described later must be introduced.

[0112] When acid labile groups for intramolecular and/or intermolecular crosslinking are to be introduced, the percent

proportion of crosslinking substituents is preferably up to 20 mol%, more preferably up to 10 mol%. If the percent substitution of crosslinking substituents is too high, crosslinking results in a higher molecular weight which can adversely affect dissolution, stability and resolution. It is also preferred to further introduce another non-crosslinking acid labile group into the crosslinked polymer at a percent substitution of up to 10 mol% for adjusting the dissolution rate to fall within the above range.

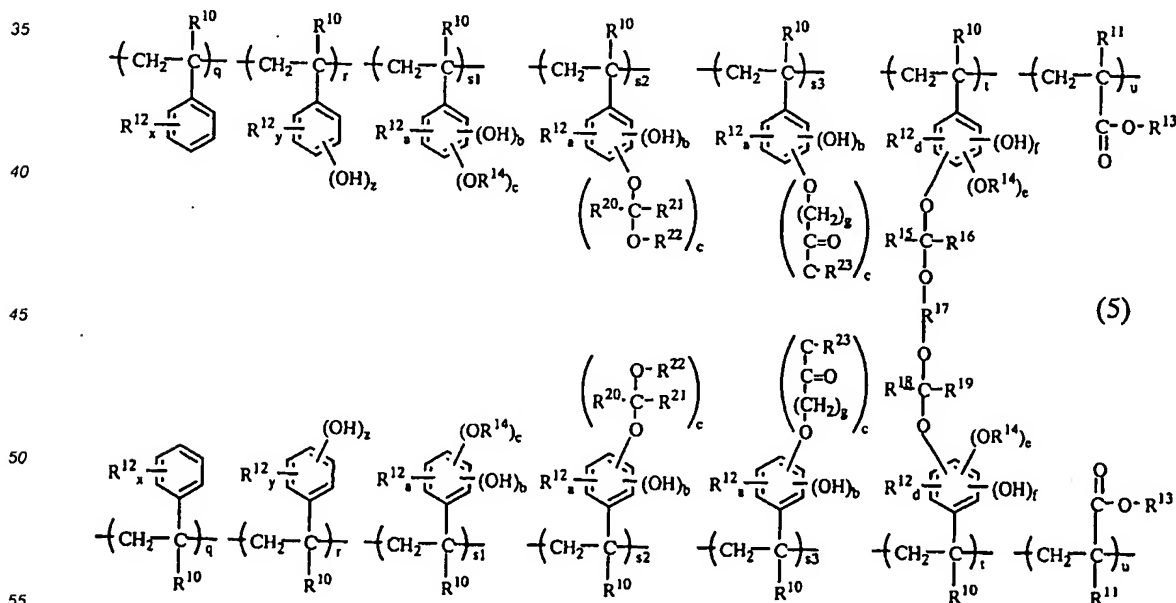
[0113] In the case of poly(p-hydroxystyrene), the optimum percent substitution differs between a substituent having a strong dissolution inhibitory action such as a tert-butoxycarbonyl group and a substituent having a weak dissolution inhibitory action such as an acetal group although the overall percent substitution is preferably 10 to 40 mol%, more preferably 20 to 30 mol%.

[0114] Polymers having such acid labile groups introduced therein should preferably have a weight average molecular weight (Mw) of 1,000 to 500,000. With a Mw of less than 1,000, polymers would perform poorly and often lack heat resistance and film formability. Polymers with a Mw of more than 500,000 would be less soluble in a developer and a resist solvent.

[0115] Where non-crosslinking acid labile groups are introduced, the polymer should preferably have a dispersity (Mw/Mn) of up to 3.5, preferably up to 1.5. A polymer with a dispersity of more than 3.5 often results in a low resolution. Where crosslinking acid labile groups are introduced, the starting alkali-soluble resin should preferably have a dispersity (Mw/Mn) of up to 1.5, and the dispersity is preferably kept at 3 or lower even after protection with crosslinking acid labile groups. If the dispersity is higher than 3, dissolution, coating, storage stability and/or resolution is often poor.

[0116] To impart a certain function, suitable substituent groups may be introduced into some of the phenolic hydroxyl and carboxyl groups on the acid labile group-protected polymer. Exemplary are substituent groups for improving adhesion to the substrate, non-acid-labile groups for adjusting dissolution in an alkali developer, and substituent groups for improving etching resistance. Illustrative, non-limiting, substituent groups include 2-hydroxyethyl, 2-hydroxypropyl, methoxymethyl, methoxycarbonyl, ethoxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, 4-methyl-2-oxo-4-oxoranyl, 4-methyl-2-oxo-4-oxanyl, methyl, ethyl, propyl, n-butyl, sec-butyl, acetyl, pivaloyl, adamantyl, isobornyl, and cyclohexyl.

[0117] In a further illustrative and preferred embodiment, the base resin (B) is a polymer represented by the following general formula (5), that is a polymer comprising recurring units of the general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and/or some of the hydrogen atoms of the remaining phenolic hydroxyl groups are eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in formula (3). The polymer has a weight average molecular weight of 1,000 to 500,000.



[0118] Herein R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , x, y, z, a, b, c, d, e, and f are as defined above.

[0119] R²¹ and R²² are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 8 carbon atoms.

R²³ is a monovalent hydrocarbon group of 1 to 18 carbon atoms which may have a hetero atom, a pair of R²¹ and R²², a pair of R²¹ and R²³ or a pair of R²² and R²³, taken together, may form a ring, each of R²¹, R²² and R²³ is a straight or branched alkylene group of 1 to 8 carbon atom when they form a ring, and R²⁴ is a tertiary alkyl group of 4 to 20 carbon atoms.

[0120] The letter g is 0 or a positive integer of 1 to 6, q, s₁, s₂, s₃, t and u are 0 or positive numbers, r is a positive number, satisfying

$$0 \leq q/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 \leq s_1/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 \leq s_2/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 \leq s_3/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 < (s_1+s_2+s_3)/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 \leq t/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 \leq u/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 < (r+s_1+s_2+s_3+t)/(q+r+s_1+s_2+s_3+t+u) \leq 1, \text{ and}$$

$$0 < r/(q+r+s_1+s_2+s_3+t+u) \leq 0.8.$$

(C) Photoacid generator

[0121] Illustrative examples of the photoacid generator include:

onium salts such as diphenyliodonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)phenyliodonium trifluoromethanesulfonate, diphenyliodonium p-toluenesulfonate, (p-tert-butoxyphenyl)phenyliodonium p-toluenesulfonate, triphenylsulfonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium trifluoromethanesulfonate, bis(p-tert-butoxyphenyl)phenylsulfonium trifluoromethanesulfonate, tris(p-tert-butoxyphenyl)sulfonium trifluoromethanesulfonate, triphenylsulfonium p-toluenesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium p-toluenesulfonate, bis(p-tert-butoxyphenyl)phenylsulfonium p-toluenesulfonate, tris(p-tert-butoxyphenyl)sulfonium p-toluenesulfonate, triphenylsulfonium nonafluorobutanesulfonate, triphenylsulfonium butanesulfonate, trimethylsulfonium trifluoromethanesulfonate, trimethylsulfonium p-toluenesulfonate, cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate, cyclohexylmethyl(2-oxocyclohexyl)sulfonium p-toluenesulfonate, dimethylphenylsulfonium trifluoromethanesulfonate, dimethylphenylsulfonium p-toluenesulfonate, dicyclohexylphenylsulfonium trifluoromethanesulfonate, and dicyclohexylphenylsulfonium p-toluenesulfonate;

β-ketosulfone derivatives such as 2-cyclohexylcarbonyl-2-(p-toluenesulfonyl)propane and 2-isopropylcarbonyl-2-(p-toluenesulfonyl)propane;

diazomethane derivatives such as bis(benzenesulfonyl)-diazomethane, bis(p-toluenesulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(n-butylsulfonyl)-diazomethane, bis(isobutylsulfonyl)diazomethane, bis(sec-butylsulfonyl)diazomethane, bis(n-propylsulfonyl)-diazomethane, bis(isopropylsulfonyl)diazomethane, and bis(tert-butylsulfonyl)diazomethane;

disulfone derivatives such as diphenyl disulfone and dicyclohexyl disulfone;

nitrobenzyl sulfonate derivatives such as 2,6-dinitrobenzyl p-toluenesulfonate and 2,4-dinitrobenzyl p-toluenesulfonate;

sulfonic acid ester derivatives such as 1,2,3-tris(methanesulfonyloxy)benzene, 1,2,3-tris(trifluoromethanesulfonyloxy)benzene, and 1,2,3-tris(p-toluenesulfonyloxy)benzene; and

imidoyl sulfonate derivatives such as phthalimidoyl triflate, phthalimidoyl tosylate, 5-norbornene-2,3-dicarboxyimidoyl triflate, 5-norbornene-2,3-dicarboxyimidoyl tosylate, and 5-norbornene-2,3-dicarboxyimidoyl n-butylsulfonate.

[0122] Preferred among these photoacid generators are onium salts such as triphenylsulfonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium trifluoromethanesulfonate, tris(p-tert-butoxyphenyl)sulfonium trifluoromethanesulfonate, triphenylsulfonium p-toluenesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium p-toluenesul-

fonate, and tris(p-tert-butoxyphenyl)sulfonium p-toluenesulfonate; and diazomethane derivatives such as bis(benzenesulfonyl)-diazomethane, bis(p-toluenesulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(n-butylsulfonyl)-diazomethane, bis(isobutylsulfonyl)diazomethane, bis(sec-butylsulfonyl)diazomethane, bis(n-propylsulfonyl)-diazomethane, bis(isopropylsulfonyl)diazomethane, and bis(tert-butylsulfonyl)diazomethane. These photoacid generators may be used singly or in combinations of two or more thereof. Onium salts are effective for improving rectangularity, while diazomethane derivatives are effective for reducing standing waves. The combination of an onium salt with a diazomethane allows for fine adjustment of the profile.

[0123] The photoacid generator is preferably added in an amount of about 0.5 to 15 parts by mass, and especially about 1 to 8 parts by mass, per 100 parts by mass of all the base resins. At less than 0.5 part, the sensitivity would be poor. The addition of more than 15 parts would lower the alkali dissolution rate, resulting in a poor resolution, and the resist becomes less heat resistant because of an increased content of monomer components.

(D) Basic compound

[0124] Examples of basic compounds include primary, secondary, and tertiary aliphatic amines, mixed amines, aromatic amines, heterocyclic amines, carboxyl group-bearing nitrogenous compounds, sulfonyl group-bearing nitrogenous compounds, hydroxyl group-bearing nitrogenous compounds, hydroxyphenyl group-bearing nitrogenous compounds, alcoholic nitrogenous compounds, amide derivatives, and imide derivatives, with the aliphatic amines being preferred.

[0125] Examples of suitable primary aliphatic amines include ammonia, methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, iso-butylamine, sec-butylamine, tertbutylamine, pentylamine, tert-amylamine, cyclopentylamine, hexylamine, cyclohexylamine, heptylamine, octylamine, nonylamine, decylamine, dodecylamine, cetylamine, methylenediamine, ethylenediamine, and tetraethylenepentamine. Examples of suitable secondary aliphatic amines include dimethylamine, diethylamine, di-n-propylamine, di-iso-propylamine, di-n-butylamine, di-iso-butylamine, di-sec-butylamine, dipentylamine, dicyclopentylamine, dihexylamine, dicyclohexylamine, diheptylamine, dioctylamine, dinonylamine, didecylamine, didodecylamine, dicetylamine, N,N-dimethylmethylenediamine, N,N-dimethylethylenediamine, and N,N-dimethyltetraethylenepentamine. Examples of suitable tertiary aliphatic amines include trimethylamine, triethylamine, tri-n-propylamine, tri-iso-propylamine, tri-n-butylamine, tri-iso-butylamine, tri-sec-butylamine, tripentylamine, tricyclopentylamine, trihexylamine, tricyclohexylamine, triheptylamine, trioctylamine, trinonylamine, tridecylamine, tridodecylamine, tricetylamine, N,N,N',N'-tetramethylmethylenediamine, N,N,N',N'-tetramethylethylenediamine, and N,N,N',N'-tetramethyltetraethylenepentamine.

[0126] Examples of suitable mixed amines include dimethylethylamine, methylethylpropylamine, benzylamine, phenethylamine, and benzyldimethylamine. Examples of suitable aromatic and heterocyclic amines include aniline derivatives (e.g., aniline, N-methylaniline, N-ethylaniline, N-propylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, ethylaniline, propylaniline, trimethylaniline, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline, 2,6-dinitroaniline, 3,5-dinitroaniline, and N,N-dimethyltoluidine), diphenyl(p-tolyl)amine, methyldiphenylamine, triphenylamine, phenylenediamine, naphthylamine, diaminonaphthalene, pyrrole derivatives (e.g., pyrrole, 2H-pyrrole, 1-methylpyrrole, 2,4-dimethylpyrrole, 2,5-dimethylpyrrole, and N-methylpyrrole), oxazole derivatives (e.g., oxazole and isooxazole), thiazole derivatives (e.g., thiazole and isothiazole), imidazole derivatives (e.g., imidazole, 4-methylimidazole, and 4-methyl-2-phenylimidazole), pyrazole derivatives, furazan derivatives, pyrroline derivatives (e.g., pyrroline and 2-methyl-1-pyrroline), pyrrolidine derivatives (e.g., pyrrolidine, N-methylpyrrolidine, pyrrolidinone, and N-methylpyrrolidinone), imidazoline derivatives, imidazolidine derivatives, pyridine derivatives (e.g., pyridine, methylpyridine, ethylpyridine, propylpyridine, butylpyridine, 4-(1-butylpentyl)pyridine, dimethylpyridine, trimethylpyridine, triethylpyridine, phenylpyridine, 3-methyl-2-phenylpyridine, 4-tert-butylpyridine, diphenylpyridine, benzylpyridine, methoxypyridine, butoxypyridine, dimethoxypyridine, 1-methyl-2-pyridone, 4-pyrrolidinopyridine, 1-methyl-4-phenylpyridine, 2-(1-ethylpropyl)pyridine, aminopyridine, and dimethylaminopyridine), pyridazine derivatives, pyrimidine derivatives, pyrazine derivatives, pyrazoline derivatives, pyrazolidine derivatives, piperidine derivatives, piperazine derivatives, morpholine derivatives, indole derivatives, isoindole derivatives, 1H-indazole derivatives, indoline derivatives, quinoline derivatives (e.g., quinoline and 3-quinolinecarbonitrile), isoquinoline derivatives, cinnoline derivatives, quinoxaline derivatives, quinoxaline derivatives, phthalazine derivatives, purine derivatives, pteridine derivatives, carbazole derivatives, phenanthridine derivatives, acridine derivatives, phenazine derivatives, 1,10-phenanthroline derivatives, adenine derivatives, adenosine derivatives, guanine derivatives, guanosine derivatives, uracil derivatives, and uridine derivatives.

[0127] Examples of suitable carboxyl group-bearing nitrogenous compounds include aminobenzoic acid, indolecarboxylic acid, and amino acid derivatives (e.g. nicotinic acid, alanine, arginine, aspartic acid, glutamic acid, glycine, histidine, isoleucine, glycyllucine, leucine, methionine, phenylalanine, threonine, lysine, 3-aminopyrazine-2-carboxylic acid, and methoxyalanine). Examples of suitable sulfonyl group-bearing nitrogenous compounds include 3-pyridinesulfonic acid and pyridinium p-toluenesulfonate. Examples of suitable hydroxyl group-bearing nitrogenous compounds,

hydroxyphenyl group-bearing nitrogenous compounds, and alcoholic nitrogenous compounds include 2-hydroxypyridine, aminocresol, 2,4-quinolinediol, 3-indolemethanol hydrate, monoethanolamine, diethanolamine, triethanolamine, N-ethyldiethanolamine, N,N-diethyl-ethanolamine, trisopropanolamine, 2,2'-iminodiethanol, 2-aminoethanol, 3-amino-1-propanol, 4-amino-1-butanol, 4-(2-hydroxyethyl)morpholine, 2-(2-hydroxyethyl)pyridine, 1-(2-hydroxyethyl)piperazine, 1-[2-(2-hydroxyethoxy)ethyl]-piperazine, piperidine ethanol, 1-(2-hydroxyethyl)-pyrrolidine, 1-(2-hydroxyethyl)-2-pyrrolidinone, 3-piperidino-1,2-propanediol, 3-pyrrolidino-1,2-propanediol, 8-hydroxyjulolidine, 3-quinuclidinol, 3-tropanol, 1-methyl-2-pyrrolidine ethanol, 1-aziridine ethanol, N-(2-hydroxyethyl)phthalimide, and N-(2-hydroxyethyl)-isonicotinamide. Examples of suitable amide derivatives include formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, propionamide, and benzamide. Suitable imide derivatives include phthalimide, succinimide, and maleimide. Of these, triethylamine, N,N-dimethylaniline, N-methylpyrrolidone, pyridine, quinoline, nicotinic acid, triethanolamine, piperidine ethanol, N,N-dimethylacetamide and succinimide are preferred.

[0128] The basic compounds may be used alone or in admixture of two or more. The basic compound is preferably formulated in an amount of 0.01 to 2 parts, and especially 0.01 to 1 part by mass, per 100 parts by mass of the base resin. Less than 0.01 part of the basic compound fails to achieve the desired effects thereof, while the use of more than 2 parts would result in too low a sensitivity.

Other components

[0129] The resist composition of the invention may include, as an optional ingredient, a surfactant which is commonly used for improving the coating characteristics. Optional ingredients may be added in conventional amounts so long as this does not compromise the objects of the invention.

[0130] Nonionic surfactants are preferred, examples of which include perfluoroalkylpolyoxyethylene ethanols, fluorinated alkyl esters, perfluoroalkylamine oxides, and fluorinated organosiloxane compounds. Useful surfactants are commercially available under the trade names Florade FC-430 and FC-431 from Sumitomo 3M K.K., Surflon S-141 and S-145 from Asahi Glass K.K., Unidine DS-401, DS-403 and DS-451 from Daikin Industry K.K., Megaface F-8151 from Dai-Nippon Ink & Chemicals K.K., and X-70-092 and X-70-093 from Shin-Etsu Chemical Co., Ltd. Preferred surfactants are Florade FC-430 from Sumitomo 3M K.K. and X-70-093 from Shin-Etsu Chemical Co., Ltd.

[0131] In forming a contact hole pattern using the chemically amplified positive resist composition of the invention, a known lithographic technique may be used. For example, the resist composition is applied onto a substrate such as a silicon wafer by spin coating or the like to form a resist film having a thickness of 0.5 to 2.0 μm , which is then prebaked on a hot plate at 60 to 150°C for 1 to 10 minutes, and preferably at 80 to 120°C for 1 to 5 minutes. A patterning mask having the desired contact hole pattern is then placed over the resist film, and the film exposed through the mask to an electron beam or to high-energy radiation with a wavelength of up to 300 nm such as deep-UV rays, an excimer laser, or x-rays in a dose of about 1 to 200 mJ/cm^2 , and preferably about 10 to 100 mJ/cm^2 , then post-exposure baked (PEB) on a hot plate at 60 to 150°C for 1 to 5 minutes, and preferably at 80 to 120°C for 1 to 3 minutes. Finally, development is carried out using as the developer an aqueous alkali solution, such as a 0.1 to 5% (preferably 2 to 3%) aqueous solution of tetramethylammonium hydroxide (TMAH), this being done by a conventional method such as dipping, puddling, or spraying for a period of 0.1 to 3 minutes, and preferably 0.5 to 2 minutes. These steps result in the formation of the desired pattern on the substrate.

[0132] Then the contact hole pattern film was subjected to thermal flow by heating on a hot plate. The heating temperature is preferably 100 to 200°C, and especially 100 to 150°C when a precision of hot plate heating is taken into account. The heating time is preferably 60 to 120 seconds.

[0133] The contact holes have a size of 0.20 to 0.30 μm at the end of exposure and development. By the thermal flow process, the contact holes are contracted to a size of 0.10 to 0.15 μm . The thermal flow process enables to form a miniature contact hole pattern.

[0134] Of the various types of high-energy radiation that may be used, the resist composition of the invention is best suited to fine pattern formation with, in particular, deep-UV rays having a wavelength of 254 to 193 nm, an excimer laser, x-rays, or an electron beam.

[0135] In the process involving the step of forming a contact hole pattern using a chemically amplified positive resist composition comprising a polymer as the base resin, and the thermal flow step of heat treating the contact hole pattern for contracting or miniaturizing the size of contact holes, the addition of a compound having at least two functional groups capable of crosslinking with the polymer to the resist composition enables easy control of the heat miniaturizing step. The process becomes adaptable and yields a precisely defined pattern profile, and thus enables formation of a microsize contact hole pattern for the fabrication of VLSIs.

EXAMPLE

[0136] Examples of the invention are given below by way of illustration and not by way of limitation. The term "pbm" is parts by mass, and PAG is a photoacid generator.

Examples & Comparative Examples

[0137] Resist materials were prepared in accordance with the formulation shown in Tables 1 and 2. The components used are shown below.

[0138] Polymer A: poly(p-hydroxystyrene) in which hydrogen atoms of hydroxyl groups are substituted with 30 mol% of 1-ethoxyethyl groups, having a weight average molecular weight of 12,000.

[0139] Polymer B: poly(p-hydroxystyrene) in which hydrogen atoms of hydroxyl groups are substituted with 15 mol% of 1-ethoxyethyl groups and 15 mol% of tert-butoxycarbonyl groups, having a weight average molecular weight of 12,000. Polymer C: poly(p-hydroxystyrene) in which hydrogen atoms of hydroxyl groups are substituted with 30 mol% of 1-ethoxypropyl groups, having a weight average molecular weight of 13,000.

[0140] Polymer D: poly(p-hydroxystyrene) in which hydrogen atoms of hydroxyl groups are substituted with 26 mol% of 1-ethoxypropyl groups and 10 mol% of tert-butyloxycarbonylmethyl groups, having a weight average molecular weight of 13,000.

[0141] Polymer E: poly(p-hydroxystyrene) in which hydrogen atoms of hydroxyl groups are substituted with 25 mol% of 1-ethoxypropyl groups and crosslinked with 5 mol% of 1,4-butanediol divinyl ether, having a weight average molecular weight of 14,000.

[0142] Polymer F: p-hydroxystyrene-1-ethylcyclopentyl methacrylate copolymer having a compositional ratio (molar ratio) of 70:30 and a weight average molecular weight of 11,000. Polymer G: p-hydroxystyrene-1-ethylcyclopentyl methacrylate-p-tert-butoxystyrene copolymer having a compositional ratio (molar ratio) of 60:30:10 and a weight average molecular weight of 12,000.

[0143] Polymer H: p-hydroxystyrene-p-(1-ethoxyethoxy)styrene-1-ethylcyclopentyl methacrylate copolymer having a compositional ratio (molar ratio) of 60:30:10 and a weight average molecular weight of 13,000.

[0144] Polymer I: p-hydroxystyrene-p-(1-ethoxyethoxy)styrene-tert-butyl methacrylate copolymer having a compositional ratio (molar ratio) of 60:30:10 and a weight average molecular weight of 14,000.

[0145] Polymer J: p-hydroxystyrene-p-(1-ethoxyethoxy)styrene-1-ethylcyclopentyl methacrylate copolymer having a compositional ratio (molar ratio) of 60:30:10 in which phenolic hydroxyl groups are crosslinked with 3 mol% of 1,4-butanediol divinyl ether, and having a weight average molecular weight of 13,000.

[0146] PAG1: (4-tert-butoxyphenyl)diphenylsulfonium p-toluenesulfonate

[0147] PAG2: (4-tert-butoxyphenyl)diphenylsulfonium 10-camphorsulfonate

[0148] PAG3: bis(tert-butylsulfonyl)diazomethane

[0149] PAG4: bis(cyclohexylsulfonyl)diazomethane

[0150] PAG5: bis(2,4-dimethylphenylsulfonyl)diazomethane

[0151] Basic compound I: tri-n-butylamine

Basic compound II: triethanolamine

Surfactant α : FC-430 (Sumitomo 3M K.K.)

[0152] Solvent 1: propylene glycol methyl ether acetate

[0153] Solvent 2: ethyl lactate

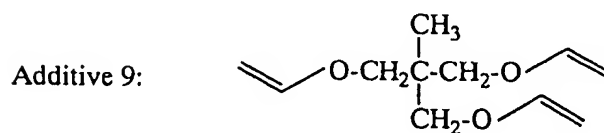
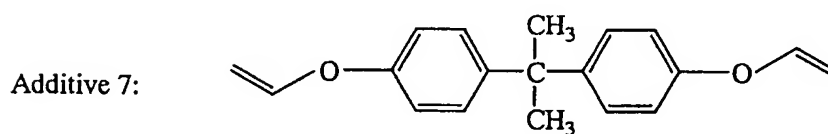
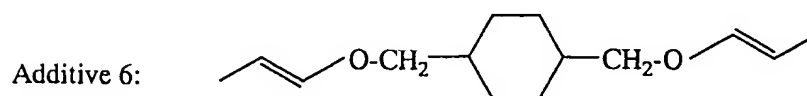
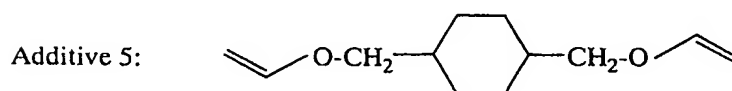
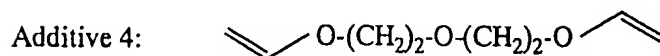
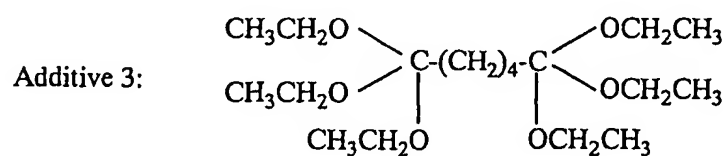
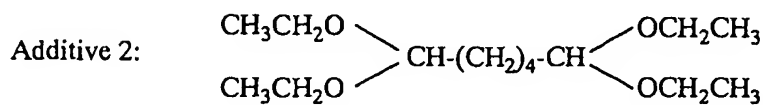
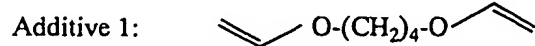
Table 1

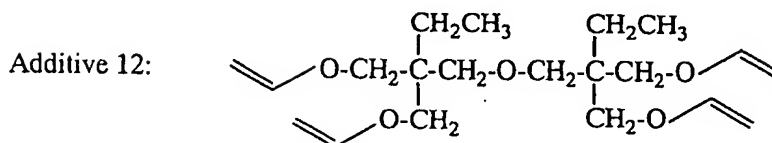
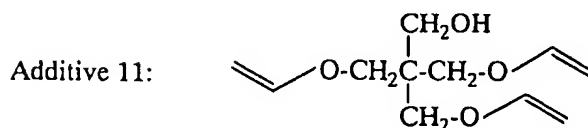
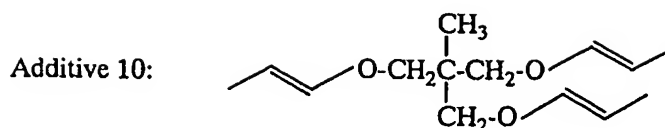
Composition (pbm)	Composition 1	Composition 2	Composition 3	Composition 4	Composition 5	Composition 6	Composition 7	Composition 8	Composition 9
Polymer A	80	80	80	-	40	-	40	-	-
Polymer B	-	-	-	80	40	-	-	-	-
Polymer C	-	-	-	-	-	80	40	40	-
Polymer D	-	-	-	-	-	-	-	40	80
Polymer E	-	-	-	-	-	-	-	-	-
Polymer F	-	-	-	-	-	-	-	-	-
Polymer G	-	-	-	-	-	-	-	-	-
Polymer H	-	-	-	-	-	-	-	-	-
Polymer I	-	-	-	-	-	-	-	-	-
Polymer J	-	-	-	-	-	-	-	-	-
PAG 1	1.0	1.0	-	1.0	1.0	1.0	-	-	-
PAG 2	-	-	-	-	-	-	1.0	1.0	-
PAG 3	2.0	-	-	-	-	-	-	-	-
PAG 4	-	2.0	1.0	2.0	2.0	-	-	-	1.0
PAG 5	-	-	2.0	-	-	2.0	2.0	2.0	2.0
Basic I Compound I	-	-	-	0.20	0.20	-	-	0.20	-
Basic II Compound II	0.20	0.20	0.20	-	-	0.20	0.20	-	0.20
Surfactant α	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Solvent 1	300	300	300	300	300	300	300	300	430
Solvent 2	130	130	130	130	130	130	130	130	-

Table 2

Composition	Composition 10	Composition 11	Composition 12	Composition 13	Composition 14	Composition 15	Composition 16	Composition 17	Composition 18
Polymer A	-	-	-	-	-	-	-	-	-
Polymer B	40	40	24	-	35	-	-	-	-
Polymer C	-	-	-	-	-	-	-	-	-
Polymer D	-	-	-	-	-	-	-	-	-
Polymer E	40	40	56	-	35	-	-	-	-
Polymer F	-	-	-	80	10	-	-	-	-
Polymer G	-	-	-	-	-	80	-	-	-
Polymer H	-	-	-	-	-	-	80	-	-
Polymer I	-	-	-	-	-	-	-	80	-
Polymer J	-	-	-	-	-	-	-	-	80
PAG 1	1.0	-	-	-	-	-	-	-	-
PAG 2	-	-	-	1.0	1.0	1.0	1.0	1.0	1.0
PAG 3	-	-	-	-	-	-	-	-	-
PAG 4	2.0	1.0	1.0	-	-	-	-	-	-
PAG 5	-	2.0	2.0	-	0.6	-	-	-	-
Basic Compound I	-	-	-	-	-	-	-	-	-
Basic Compound II	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Surfactant α	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Solvent 1	300	430	430	300	300	300	300	300	300
Solvent 2	130	-	-	130	130	130	130	130	130

[0154] To the thus prepared resist solutions, compounds for controlling the flow rate in the thermal flow process according to the invention (referred to as Additive below) were added in a proportion based on the entire resist system as shown in Tables 3 to 20.





[0155] The resist material thus obtained was filtered through a 0.2- μ m Teflon filter. The resist solution was spin-coated onto a silicon wafer, then baked at 100°C for 90 seconds on a hot plate to give a resist film having a thickness of 0.77 μ m. The resist film was exposed using an excimer laser stepper NSR-S202A (Nikon K.K., NA 0.6) with a contact hole pattern reticle mounted thereon, then baked (PEB) at 110°C for 90 seconds, and developed with a solution of 2.38% TMAH in water, thereby giving a contact hole pattern. The target was contact holes having a size of 0.25 μ m and a pitch of 1:2 at the end of development.

[0156] In this way, contact hole patterns were formed by coating resist materials onto several tens of silicon wafers. Thereafter, heat treatment was carried out for thermal flow, that is, for contracting the contact holes. The heat treatment continued for 90 seconds on a hot plate while the temperature was changed at intervals of 2°C among the wafers.

[0157] The size of contact holes at the end of heat treatment was measured using a scanning electron microscope (Top Down SEM). The measured data were plotted in a graph with the heat treating temperature on the abscissa and the contact hole size on the ordinate. The contact hole size was 0.25 μ m prior to the heat treatment, and the temperature at which the contact hole size reached 0.15 μ m was determined from the graph.

[0158] Also the gradient of thermal flow (flow rate) at the 0.15 μ m size was determined from the graph. It is judged that a lower flow rate is better because the thermal flow process is more effectively controllable. Additionally, the presence of scum on the resist surface was examined under Top Down SEM and after the resist pattern was sectioned, the inclusion of scum within the resist pattern was examined under a scanning electron microscope (Cross Sectional SEM). The cross-sectional shape of contact holes was observed under Cross Sectional SEM. A composition giving perpendicular contact hole sidewalls is judged effective.

[0159] Similar resist compositions without the inventive additives are Comparative Examples. The results of evaluation are shown in Tables 21 to 38.

Table 3

Example	Resist composition	Additive	Addition amount(%)
Example 1	Composition 1	Additive 1	0.5
Example 2	Composition 1	Additive 1	0.8
Example 3	Composition 1	Additive 1	1.6
Example 4	Composition 1	Additive 2	0.5
Example 5	Composition 1	Additive 2	0.8
Example 6	Composition 1	Additive 2	1.6
Example 7	Composition 1	Additive 3	0.5
Example 8	Composition 1	Additive 3	0.8

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Table 3 (continued)

Example	Resist composition	Additive	Addition amount(%)
Example 9	Composition 1	Additive 3	1.6
Example 10	Composition 1	Additive 5	0.5
Example 11	Composition 1	Additive 5	0.8
Example 12	Composition 1	Additive 5	1.6
Example 13	Composition 1	Additive 9	0.5
Example 14	Composition 1	Additive 9	0.8
Example 15	Composition 1	Additive 9	1.6
Example 16	Composition 1	Additive 12	0.8
CE 1	Composition 1	-	0

Table 4

Example	Resist composition	Additive	Addition amount(%)
Example 17	Composition 2	Additive 6	0.8
Example 18	Composition 2	Additive 8	0.8
Example 19	Composition 2	Additive 10	0.8
CE 2	Composition 2	-	0

Table 5

Example	Resist composition	Additive	Addition amount(%)
Example 21	Composition 3	Additive 2	0.8
Example 22	Composition 3	Additive 3	0.8
Example 23	Composition 3	Additive 4	0.5
Example 24	Composition 3	Additive 4	0.8
Example 25	Composition 3	Additive 4	1.6
Example 26	Composition 3	Additive 6	1.6
Example 27	Composition 3	Additive 10	0.5
Example 28	Composition 3	Additive 10	0.8
Example 29	Composition 3	Additive 10	1.6
CE 3	Composition 3	-	0

Table 6

Example	Resist composition	Additive	Addition amount(%)
Example 30	Composition 4	Additive 5	1.6
CE 4	Composition 4	-	0

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Table 7

Example	Resist composition	Additive	Addition amount(%)
Example 31	Composition 5	Additive 1	1.6
Example 32	Composition 5	Additive 2	1.6
Example 33	Composition 5	Additive 3	1.6
Example 34	Composition 5	Additive 5	1.6
Example 35	Composition 5	Additive 7	1.6
Example 36	Composition 5	Additive 8	1.6
Example 37	Composition 5	Additive 9	1.6
CE 5	Composition 5	-	0

Table 8

Example	Resist composition	Additive	Addition amount(%)
Example 38	Composition 6	Additive 1	1.6
Example 39	Composition 6	Additive 2	1.6
Example 40	Composition 6	Additive 3	1.6
Example 41	Composition 6	Additive 6	1.6
Example 42	Composition 6	Additive 7	1.6
Example 43	Composition 6	Additive 8	1.6
Example 44	Composition 6	Additive 11	1.6
CE 6	Composition 6	-	0

Table 9

Example	Resist composition	Additive	Addition amount(%)
Example 45	Composition 7	Additive 1	2.4
Example 46	Composition 7	Additive 2	2.4
Example 47	Composition 7	Additive 3	2.4
Example 48	Composition 7	Additive 5	2.4
Example 49	Composition 7	Additive 9	1.6
Example 50	Composition 7	Additive 12	1.6
CE 7	Composition 7	-	0

Table 10

Example	Resist composition	Additive	Addition amount(%)
Example 51	Composition 8	Additive 10	0.8
CE 8	Composition 8	-	0

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Table 11

Example	Resist composition	Additive	Addition amount(%)
Example 52	Composition 9	Additive 5	0.8
Example 53	Composition 9	Additive 11	0.8
CE 9	Composition 9	-	0

Table 12

Example	Resist composition	Additive	Addition amount(%)
Example 54	Composition 10	Additive 1	1.6
Example 55	Composition 10	Additive 2	1.6
Example 56	Composition 10	Additive 3	1.6
Example 57	Composition 10	Additive 5	1.6
Example 58	Composition 10	Additive 10	1.6
CE 10	Composition 10	-	0

Table 13

Example	Resist composition	Additive	Addition amount(%)
Example 59	Composition 11	Additive 1	1.6
Example 60	Composition 11	Additive 2	1.6
Example 61	Composition 11	Additive 3	1.6
Example 62	Composition 11	Additive 5	1.6
Example 63	Composition 11	Additive 10	1.6
CE 11	Composition 11	-	0

Table 14

Example	Resist composition	Additive	Addition amount(%)
Example 64	Composition 12	Additive 1	1.6
Example 65	Composition 12	Additive 2	1.6
Example 66	Composition 12	Additive 3	1.6
Example 67	Composition 12	Additive 5	1.6
Example 68	Composition 12	Additive 10	1.6
CE 12	Composition 12	-	0

Table 15

Example	Resist composition	Additive	Addition amount(%)
Example 69	Composition 13	Additive 6	1.6
Example 70	Composition 13	Additive 10	1.6
CE 13	Composition 13	-	0

Table 16

Example	Resist composition	Additive	Addition amount(%)
Example 71	Composition 14	Additive 6	1.6
Example 72	Composition 14	Additive 10	1.6
Example 73	Composition 14	Additive 12	0.8
CE 14	Composition 14	-	0

Table 17

Example	Resist composition	Additive	Addition amount(%)
Example 74	Composition 15	Additive 6	1.6
Example 75	Composition 15	Additive 10	1.6
CE 15	Composition 15	-	0

Table 18

Example	Resist composition	Additive	Addition amount(%)
Example 76	Composition 16	Additive 6	1.6
Example 77	Composition 16	Additive 10	0.8
CE 16	Composition 16	-	0

Table 19

Example	Resist composition	Additive	Addition amount(%)
Example 78	Composition 17	Additive 6	1.6
Example 79	Composition 17	Additive 10	0.8
CE 17	Composition 17	-	0

Table 20

Example	Resist composition	Additive	Addition amount(%)
Example 80	Composition 18	Additive 6	1.6
Example 81	Composition 18	Additive 10	0.8
CE 18	Composition 18	-	0

[0160] In the following Tables, the "heating temperature" is the heating temperature for thermal flow at which the contact hole of 0.25 μm size was contracted to 0.15 μm ; and the "contact hole shape" is the cross-sectional shape of contact holes after the thermal flow.

Table 21

	Heating Temperature($^{\circ}\text{C}$)	Flow rate ($\text{nm}/^{\circ}\text{C}$)	Scum on or in resist pattern	Contact hole shape
Example 1	128	12.5	nil	slightly bowed
Example 2	128	11.4	nil	perpendicular
Example 3	126	8.6	nil	perpendicular

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Table 21 (continued)

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 4	124	16.5	nil	slightly bowed
Example 5	124	13.0	nil	perpendicular
Example 6	124	11.1	nil	perpendicular
Example 7	124	16.1	nil	slightly bowed
Example 8	124	14.0	nil	perpendicular
Example 9	122	10.8	nil	perpendicular
Example 10	126	12.1	nil	slightly bowed
Example 11	126	11.0	nil	perpendicular
Example 12	126	10.0	nil	perpendicular
Example 13	124	9.0	some scum observed	perpendicular
Example 14	124	7.3	some scum observed	perpendicular
Example 15	122	5.4	some scum observed	perpendicular
Example 16	120	5.3	some scum observed	perpendicular
CE 1	130	19.0	nil	bowed

Table 22

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 17	126	11.2	nil	perpendicular
Example 18	126	11.1	nil	perpendicular
Example 19	126	5.8	nil	perpendicular
CE 2	130	19.0	nil	bowed

Table 23

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 20	120	10.1	nil	perpendicular
Example 21	120	10.3	nil	perpendicular
Example 22	120	13.8	nil	slightly bowed
Example 23	120	12.6	nil	perpendicular
Example 24	118	10.0	nil	perpendicular
Example 25	126	8.9	nil	perpendicular
Example 26	118	9.0	nil	perpendicular
Example 27	118	7.8	some scum observed	perpendicular
Example 28	116	5.4	some scum observed	perpendicular
CE 3	124	19.2	nil	bowed

Table 24

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 29	160	8.8	nil	perpendicular
CE 4	162	17.8	nil	bowed

Table 25

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	contact hole shape
Example 30	154	8.0	nil	perpendicular
Example 31	154	8.2	nil	perpendicular
Example 32	154	8.3	nil	perpendicular
Example 33	152	8.8	nil	perpendicular
Example 34	150	10.1	nil	perpendicular
Example 35	148	9.2	nil	perpendicular
Example 36	148	5.0	some scum observed	perpendicular
CE 5	162	18.1	nil	bowed

Table 26

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	contact hole shape
Example 37	128	8.0	nil	perpendicular
Example 38	128	8.2	nil	perpendicular
Example 39	128	8.3	nil	perpendicular
Example 40	126	8.8	nil	perpendicular
Example 41	130	10.1	nil	perpendicular
Example 42	130	9.2	nil	perpendicular
Example 43	126	5.0	some scum observed	perpendicular
CE 6	128	19.4	nil	bowed

Table 27

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 44	124	6.3	nil	perpendicular
Example 45	124	6.4	nil	perpendicular
Example 46	122	6.5	nil	perpendicular
Example 47	120	5.9	nil	perpendicular
Example 48	126	5.9	some scum observed	perpendicular
Example 49	128	4.0	scum observed	perpendicular
CE 7	126	19.5	nil	bowed

Table 28

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 50	148	7.3	nil	perpendicular
CE 8	146	18.8	nil	bowed

Table 29

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 51	138	11.6	nil	perpendicular
Example 52	132	7.5	nil	perpendicular
CE 9	136	19.3	nil	bowed

Table 30

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 53	148	8.7	nil	perpendicular
Example 54	148	8.8	nil	perpendicular
Example 55	148	9.2	nil	perpendicular
Example 56	146	8.5	nil	perpendicular
Example 57	146	5.4	some scum observed	perpendicular
CE 10	144	17.0	nil	bowed

Table 31

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 58	150	8.9	nil	perpendicular
Example 59	150	9.1	nil	perpendicular
Example 60	150	9.7	nil	perpendicular
Example 61	148	8.8	nil	perpendicular
Example 62	146	5.5	some scum observed	perpendicular
CE 11	146	17.2	nil	bowed

Table 32

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 63	147	8.4	nil	perpendicular
Example 64	149	8.5	nil	perpendicular
Example 65	149	9.3	nil	perpendicular
Example 66	149	8.6	nil	perpendicular
Example 67	153	5.6	some scum observed	perpendicular

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Table 32 (continued)

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
5 CE 12	152	18.0	nil	bowed

Table 33

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
10 Example 68	176	7.9	nil	perpendicular
Example 69	178	3.9	nil	perpendicular
15 CE 13	176	17.8	nil	bowed

Table 34

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
20 Example 70	160	9.0	nil	perpendicular
Example 71	154	5.1	some scum observed	perpendicular
25 Example 72	158	4.9	some scum observed	perpendicular
CE 14	158	16.9	nil	bowed

Table 35

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
30 Example 73	180	9.3	nil	perpendicular
35 Example 74	180	5.4	some scum observed	perpendicular
CE 15	180	17.3	nil	bowed

Table 36

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
40 Example 75	156	8.5	nil	perpendicular
Example 76	156	7.0	some scum observed	perpendicular
45 CE 16	156	17.0	nil	bowed

Table 37

	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
50 Example 77	162	8.5	nil	perpendicular
Example 78	156	7.2	some scum observed	perpendicular
55 CE 17	160	17.8	nil	bowed

Table 38

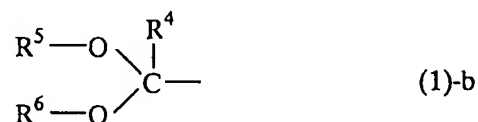
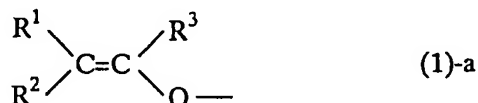
	Heating Temperature(°C)	Flow rate (nm/°C)	Scum on or in resist pattern	Contact hole shape
Example 79	146	7.8	nil	perpendicular
Example 80	150	7.4	some scum observed	perpendicular
CE 18	152	17.4	nil	bowled

[0161] Japanese Patent Application No. 11-323332 is incorporated herein by reference.

[0162] Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

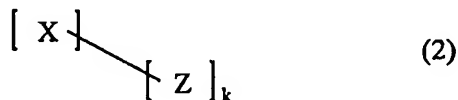
Claims

1. A chemically amplified positive resist composition for forming a contact hole pattern by the thermal flow process, comprising a compound containing at least two functional groups of the general formulas (1)-a to (1)-c in a molecule,



wherein R¹ to R⁴ are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, R⁵ to R⁹ are independently straight, branched or cyclic alkyl groups of 1 to 12 carbon atoms, and a pair of R¹ and R³, a pair of R⁴ and R⁵, a pair of R⁵ and R⁶, a pair of R⁷ and R⁸, a pair of R⁷ and R⁹ or a pair of R⁸ and R⁹, taken together, may form a ring.

2. The resist composition of claim 1 wherein the compound containing at least two functional groups has the general formula (2):



wherein Z is a functional group selected from the formulas (1)-a to (1)-c, the Z's may be the same or different, k is a positive integer of 2 to 6, and X is a k-valent organic group of 2 to 20 carbon atoms.

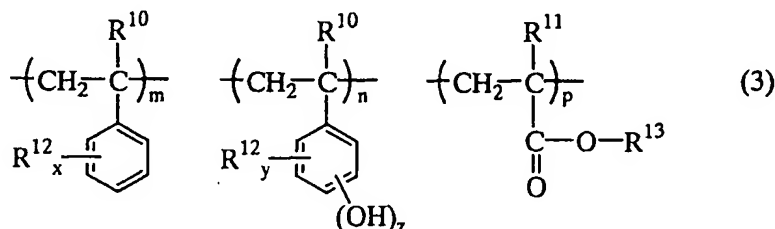
3. The resist composition of claim 2 wherein the compound containing at least two functional groups of the general

formula (2) is present in an amount of 0.1 to 5% by mass of the overall resist composition.

4. A chemically amplified positive resist composition for forming a contact hole pattern by the thermal flow process, comprising

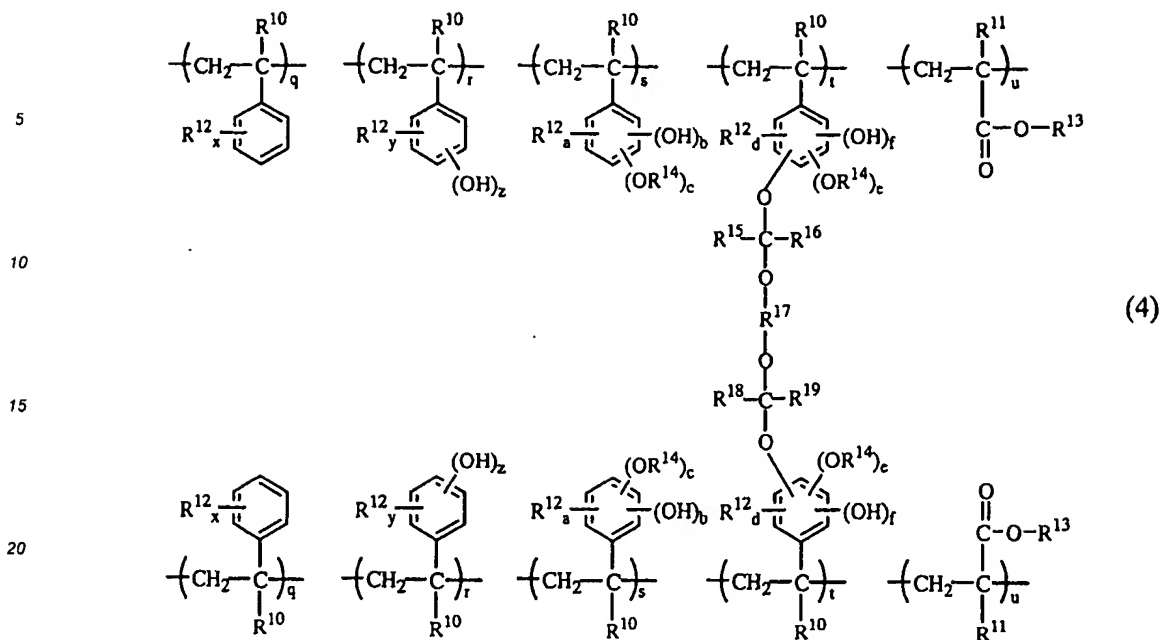
- (A) an organic solvent,
 (B) a base resin in the form of a polymer having acid labile groups,
 (C) a photoacid generator,
 (D) a basic compound, and
 (E) a compound containing at least two functional groups of the general formulas (1)-a to (1)-c in a molecule, as set forth in claim 1.

5. The resist composition of claim 4 wherein the base resin (B) is a polymer comprising recurring units of the following general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and some of the hydrogen atoms of the remaining phenolic hydroxyl groups are optionally eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in the formula (3), said polymer having a weight average molecular weight of 1,000 to 500,000.



wherein R¹⁰ is hydrogen or methyl, R¹¹ is hydrogen or a methyl, phenyl or cyano group, R¹² is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms, R¹³ is hydrogen or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, x is 0 or a positive integer of up to 5, y and z are positive integers satisfying y+z ≤ 5, m and p are 0 or positive numbers, n is a positive number, satisfying 0 ≤ m/(m+n+p) ≤ 0.8, 0 < n/(m+n+p) ≤ 1, and 0 ≤ p/(m+n+p) ≤ 0.8.

6. The resist composition of claim 5 wherein the base resin (B) is a polymer represented by the following general formula (4), that is a polymer comprising recurring units of the general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and some of the hydrogen atoms of the remaining phenolic hydroxyl groups are optionally eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in formula (3), said polymer having a weight average molecular weight of 1,000 to 500,000.

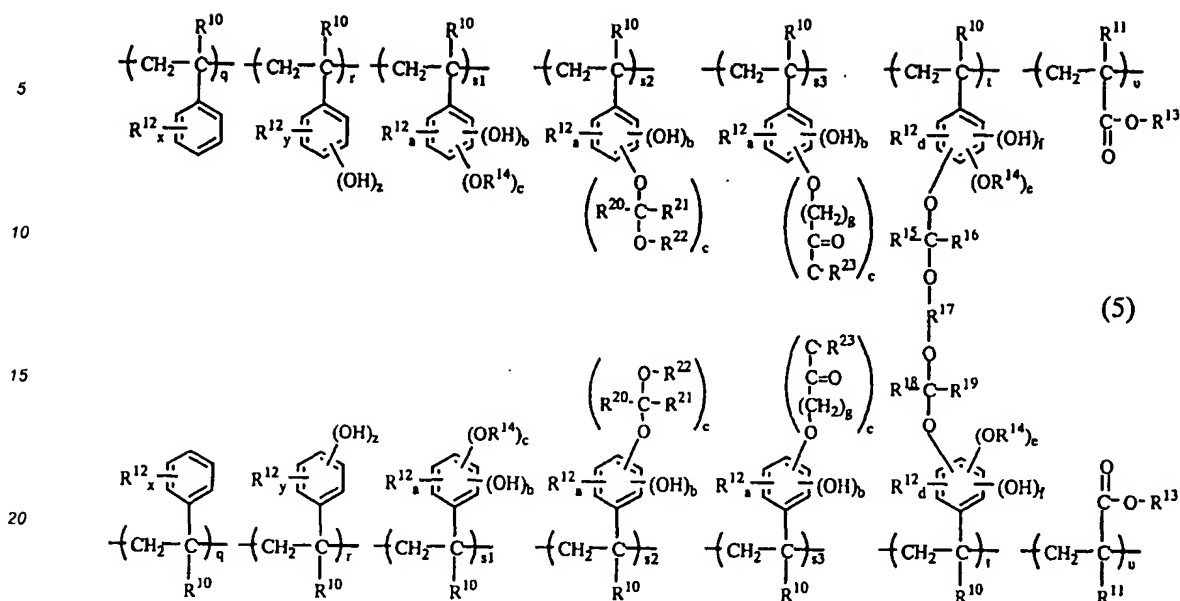


wherein R¹⁰ is hydrogen or methyl, R¹¹ is hydrogen or a methyl, phenyl or cyano group, R¹² is a straight, branched or cyclic alkyl group of 1 to 8 carbon atoms, R¹³ is hydrogen or a straight, branched or cyclic alkyl group of 1 to 10 carbon atoms, R¹⁴ is an acid labile group of at least one type, R¹⁵, R¹⁶, R¹⁸ and R¹⁹ are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 6 carbon atoms, and R¹⁷ is a divalent or polyvalent hydrocarbon group of 1 to 10 carbon atoms which may be separated by an oxygen atom, each said unit may be constructed of one type or at least two types,

x is 0 or a positive integer of up to 5, y and z are positive integers satisfying $y+z \leq 5$, a, b and c are positive integers satisfying $a+b+c \leq 5$, with the proviso that c is not equal to 0, d, e and f are 0 or positive integers satisfying $d+e+f \leq 4$.

q, t and u are 0 or positive numbers, r and s are positive numbers, satisfying $0 \leq q/(q+r+s+t+u) \leq 0.8$, $0 < s/(q+r+s+t+u) \leq 0.8$, $0 \leq t/(q+r+s+t+u) \leq 0.8$, $0 \leq u/(q+r+s+t+u) \leq 0.8$, $0 < (r+s+t)/(q+r+s+t+u) \leq 1$, and $0 < r/(q+r+s+t+u) \leq 0.8$.

7. The resist composition of claim 6 wherein the base resin (B) is a polymer represented by the following general formula (5), that is a polymer comprising recurring units of the general formula (3) in which some of the hydrogen atoms of the phenolic hydroxyl groups are partially replaced by acid labile groups of at least one type, and some of the hydrogen atoms of the remaining phenolic hydroxyl groups are optionally eliminated for crosslinkage within a molecule and/or between molecules with crosslinking groups having C-O-C linkages, the total of the acid labile groups and the crosslinking groups being more than 0 mol% to 80 mol% of the entire hydrogen atoms of phenolic hydroxyl groups in formula (3), said polymer having a weight average molecular weight of 1,000 to 500,000.



25 wherein R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, x, y, z, a, b, c, d, e, and f are as defined above, R²¹ and R²² are independently hydrogen or straight, branched or cyclic alkyl groups of 1 to 8 carbon atoms, R²³ is a monovalent hydrocarbon group of 1 to 18 carbon atoms which may have a hetero atom, a pair of R²¹ and R²², a pair of R²¹ and R²³ or a pair of R²² and R²³, taken together, may form a ring, each of R²¹, R²² and R²³ is a straight or branched alkylene group of 1 to 8 carbon atom when they form a ring, R²⁴ is a tertiary alkyl group of 4 to 20 carbon atoms, g is 0 or a positive integer of 1 to 6, q, s₁, s₂, s₃, t and u are 0 or positive numbers, r is a positive number, satisfying

$$0 \leq q/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

35 $0 \leq s_1/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$

$$0 \leq s_2/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

40 $0 \leq s_3/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$

$$0 < (s_1+s_2+s_3)/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

$$0 \leq t/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$$

45 $0 \leq u/(q+r+s_1+s_2+s_3+t+u) \leq 0.8,$

$$0 < (r+s_1+s_2+s_3+t)/(q+r+s_1+s_2+s_3+t+u) \leq 1, \text{ and}$$

$$0 < r/(q+r+s_1+s_2+s_3+t+u) \leq 0.8.$$

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8. The resist composition of claim 4 wherein component (C) is an onium salt or diazomethane derivative or both.

9. The resist composition of claim 4 wherein component (D) is an aliphatic amine.

55 10. A method for forming a contact hole pattern, comprising the steps of

(i) applying the chemically amplified positive resist composition of any one of claims 1 to 9 onto a substrate to form a coating,

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(ii) heat treating the coating and exposing the coating to high energy radiation with a wavelength of up to 300 nm or electron beam through a photo-mask,

(iii) optionally heat treating the exposed coating, and developing the coating with a developer, thereby forming a contact hole pattern, and

5 (iv) further heat treating the contact hole pattern for reducing the size of contact holes.

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FIG.1

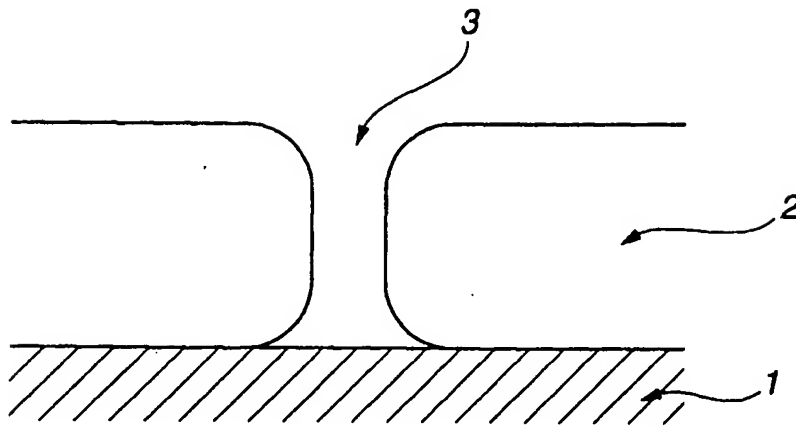


FIG.2

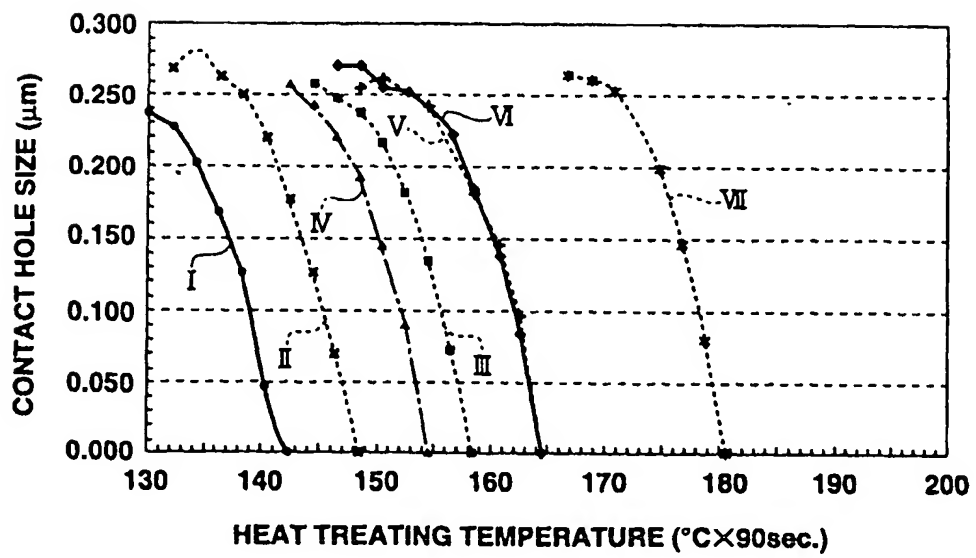
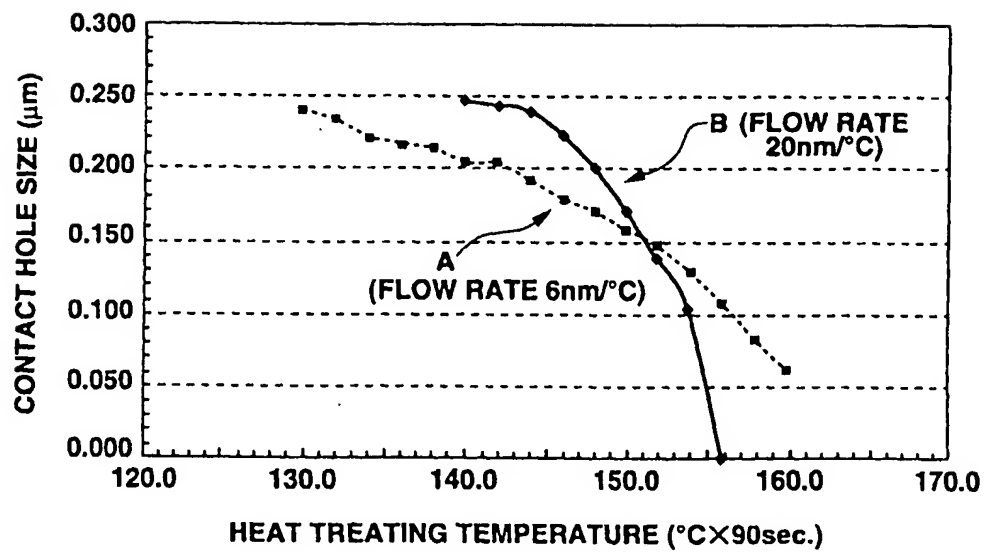


FIG.3





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 31 0001

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X	US 5 496 678 A (G. IMAI ET AL.) 5 March 1996 (1996-03-05) * column 5, line 38 - line 63 * * column 6, line 1-6 * * claims; example 1 *	1-3	
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X	DATABASE WPI Section Ch, Week 199427 Derwent Publications Ltd., London, GB; Class A26, AN 1994-223188 XP002159382 & JP 06 161110 A (NITTO DENKO CORP), 7 June 1994 (1994-06-07) * abstract *	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.7) G03F
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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p>			

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05-02-2001

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